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The purpose of this investigation was to collect, review, evaluate, and present existing information to determine whether a sufficient data base is available to develop corrosion control regulations for the water works industry as required by the Safe Drinking Water Act. To accomplish this objective, an exhaustive literature search was completed which included a review of the various materials used in the water works industry and their corrosion characteristics. Results of laboratory and field research on each material as related to corrosion in the water works industry are extensively reviewed and data is presented as appropriate. Major emphasis is placed on assessing the conditions of service and water quality characteristics in potable water systems on the corrosion or deterioration of each material. A review of corrosion monitoring and detection techniques is given which addresses the various methodologies used to identify and evaluate corrosive waters. Available corrosion prevention and control techniques are also evaluated and presented. Additionally, case histories of corrosion control programs are presented for examples. Finally, the information and data presented in these reviews are compiled and presented in tabular form. These tables provide an overall view of the nature of the corrosion problems in the water works industry and can be used as a guide for the initial consideration of corrosion control regulations.

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FINAL REPORT

CORROSION IN POTABLE WATER SYSTEMS

Contract No. 68-01-5834

Prepared by:

David W. DeBerry
James R. Kidwell
David A. Malish

SumX Corporation
P.O. Box 14864/1300 E. Braker Ln.
Austin, Texas 78761

February 1982

PROJECT OFFICER:

Mr. Peter Lassovszky
Science and Technology Branch
Criteria & Standards Division, ODW (WH-550)
U.S. Environmental Protection Agency
401 M Street, SW
Washington, D.C. 20460

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ABSTRACT

The purpose of this investigation was to collect, review, evaluate, and present existing information to determine whether a sufficient data base is available to develop corrosion control regulations for the water works industry as required by the Safe Drinking Water Act. To accomplish this objective, an exhaustive literature search was completed which included a review of the various materials used in the water works industry and their corrosion characteristics. Results of laboratory and field research on each material as related to corrosion in the water works industry are extensively reviewed and data is presented as appropriate. Major emphasis is placed on assessing the conditions of service and water quality characteristics in potable water systems on the corrosion or deterioration of each material. A review of corrosion monitoring and detection techniques is given which addresses the various methodologies used to identify and evaluate corrosive waters. Available corrosion prevention and control techniques are also evaluated and presented. Additionally, case histories of corrosion control programs are presented for examples. Finally, the information and data presented in these reviews are compiled and presented in tabular form. These tables provide an overall view of the nature of the corrosion problems in the water works industry and can be used as a guide for the initial consideration of corrosion control regulations.

Corrosion in potable water systems may be caused by either inherent factors or design, construction, or operational deficiencies. Most materials used in potable water systems are susceptible to corrosion. The properties of the material and the composition of the water are interactive in the occurrence or inhibition of inherent corrosion. Corrosion susceptibility is also influenced by many other factors including temperature, local flow rate, pH, alkalinity, carbon dioxide, dissolved solids, and minor chemical constituents of either the water or corroding material. Corrosion problems may also be caused by poor choice of materials, coupling of dissimilar metals, improper installation practices, incorrect design allowing unnecessary stagnant areas or crevices, release of unstable waters, or addition of additives. Potable water distribution and plumbing systems may contain a variety of materials. The environmental conditions noted above can have effects on individual materials that differ both in type and degree and alleviation of corrosion problems for one material or type of installation could create problems with another or result in deterioration of overall water quality. Results of this study show that the nature of corrosion and possible corrosion control alternatives are extremely complex. Limiting or predicting the corrosiveness of water by the use of a universal corrosion index or parameter is not feasible at this time. Instead it appears that corrosion control can only be accomplished through a comprehensively applied program on a community water system case by case basis.

This report is submitted in fulfillment of Contract No. 68-01-5834 by SumX Corporation under the sponsorship of the U.S. Environmental Protection Agency.

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SECTION 1

INTRODUCTION

BACKGROUND

The Safe Drinking Water Act of 1974 (PL 93-523) was passed by Congress to safeguard public drinking water supplies and to protect public health. This act essentially states that National Drinking Water Regulations will be established and enforced for all public drinking water supplies. As a result, the Environmental Protection Agency (EPA) proposed National Interim Primary Drinking Water Regulations (NIPDWR) which became effective June 24, 1977. These interim regulations have established maximum allowable concentrations of various contaminants in drinking water supplies and require that water suppliers sample and analyze the water on a regular basis. Contaminants identified by the NIPDWR for limitations in drinking water supplies include bacteria, turbidity, radioactivity, trihalomethanes, ten inorganic chemicals, and six organic pesticides. These regulations will be reviewed at least once every three years and can be amended at any time.

Corrosion control regulations are addressed directly in the National Secondary Drinking Water Regulations which state that potable waters should be non-corrosive for protection of the public welfare. These Secondary Regulations are federal guidelines only, but may be adopted and enforced by individual states.

The EPA has determined that corrosive materials in the water works industry can pose a serious threat to public health and, on August 27, 1980, issued amendments to the NIPDWR which specifically outline monitoring for corrosion related parameters. These regulations require public water systems to identify the presence of specific materials of construction within the distribution systems and to monitor and report corrosivity characteristics including pH, alkalinity, hardness, total dissolved solids, and the Langelier Index. Additional regulations will be developed and enforced by EPA that set forth requirements for systems distributing corrosive waters to increase monitoring for corrosion byproducts such as lead and cadmium.

Attempts to develop regulations controlling corrosion in the water works industry is controversial owing to the complexity of the corrosion problem. Major problems include the lack of legal definition for corrosivity, the lack of a generally acceptable method for measuring corrosivity, and the lack of corrosion control methods which are effective throughout the entire distribution system as well as compatible with other potable water supply objectives. The problem is further complicated by the requirement to regulate corrosion at the "free flowing outlet of the ultimate consumer of a public water system." However, in defining maximum contaminant levels, the NIPDWR excludes contaminants added to the water under circumstances controlled by the user, except those resulting from corrosion of piping and plumbing caused by the water quality. This regulation implies that the water supplier must be cognizant of the pipe materials in the service lines and within the household as well as the distribution system.

Corrosion in potable water systems may be caused by either inherent factors or design, construction, or operational deficiencies. Most materials used in potable water systems are susceptible to corrosion in waters containing oxygen. This inherent susceptibility is often decreased by formation of protective coatings on the bare material surface. The coatings are formed by precipitation of substances such as calcium carbonate from solution or growth of insulating corrosion reaction product films on the material surface. Thus, the properties of the material and the composition of the water are interactive in the occurrence or inhibition of inherent corrosion. Corrosion susceptibility is also influenced by many other factors including temperature, local flow rate, pH, alkalinity, carbon dioxide, dissolved solids, and minor chemical constituents of either the water or corroding material.

Corrosion problems may also be caused by poor choice of materials, coupling of dissimilar metals, improper installation practices, incorrect design allowing unnecessary stagnant areas or crevices, release of unstable waters, or addition of additives. While in principle subject to correction, it is necessary to assume that many of these defects will persist for some time in present systems.

Potable water distribution and plumbing systems may contain a variety of materials. The environmental conditions noted above can have effects on individual materials that differ both in type and degree. It is possible that alleviation of corrosion problems for one material or type of installation could create problems with another or result in deterioration of overall water quality.

Before corrosion control measures can be implemented, sufficient evidence must be available which detects the presence of corrosion. Additionally, the location and cause of the corrosion occurrence must be identified. This information can be obtained through the initiation of a comprehensive monitoring program of potential corrosion byproducts. However, under existing regulations, water utilities are required to monitor only once per year for facilities using surface water sources and only once every three years for facilities using groundwater sources. The only major corrosion products required to be monitored are lead and cadmium. Thus, not only is the current monitoring schedule insufficient to reliably detect corrosion, much less to isolate the location and possible causes, but some corrosion recognized by the consumer, in terms of economics and aesthetics, may not be recognized by the water supplier.

The secondary drinking water regulations state that potable waters should be non-corrosive. No attempt has been made to assign a numerical value for a maximum contaminant level (MCL) for corrosion. A major problem in attempting to produce a "non-corrosive" water is the lack of a generally applicable measure of water corrosivity. Several corrosive or "aggressive" indices have been developed to rate and evaluate the corrosivity of potable waters. These indices include the Langelier Index, the aggressive index, the Ryznar Stability Index, the Larson Index, the Casil Index, the Riddick Index, and the driving force index. Predictions using these indices are often found to be in disagreement with field experience.

These discrepancies are often a result of the differences between theoretical deviations and actual conditions. For instance, indices predicting $CaCO_3$ deposition do not incorporate factors for metastable conditions nor do they reflect that the protective capacity of the deposit is a function of the physical and chemical conditions existing during its formation.

Development of a general index is also difficult because of the multiple roles of chemical species in potable water. The most common and abundant aggressive ions in potable waters are usually considered to be chloride and sulfate, although they may aid formation of more protective calcium carbonate scale. Also, although oxygen provides the main driving force for many types of corrosion in potable water, there is evidence that a certain minimum solution oxygen level is necessary for the initial formation of protective calcium carbonate films on steel. Flow velocities are also important for the formation of protective layers and there is some evidence that low levels of natural organic or silicate inhibitors may be influential.

Direct tests have been performed using pipe sections, metal coupons, and water quality analyses to determine corrosivity. These tests must be performed over a fairly long period of time and may be prohibitively expensive for small communities. The results of these tests are also often inconsistent with observations of field equipment and often are of limited use in isolating a specific problem.

The inconsistency between practical and theoretical measurements and field observations can be attributed to the large variety of mechanisms by which corrosion can occur. All factors which can influence or cause corrosion are not necessarily identified using indices or direct field tests. For example, pitting corrosion can be initiated from oxygen being trapped and not evenly distributed in areas within the distribution system. Corrosion from erosion or impingement caused by excessive velocities at certain areas or occasional sand discharges can remove protective films and accelerate corrosion. Increased velocities often result from improper design of home or commercial plumbing facilities.

Another problem exists with the wide range of materials and installation practices used in the water works industry. A specific water quality may be non-corrosive to some materials but corrosive to others. Most older distribution systems were constructed of cast iron pipe. Materials used more recently for distribution systems include welded steel, ductile iron, precast concrete, and asbestos cement. Asbestos cement is used most extensively today because of its excellent physical properties. However, asbestos cement pipe is limited to 30 inches in diameter and cannot be used if large hydrostatic pressures are required. Steel pipes are often used for larger diameter transmission mains and may be protected with a cement mortar coating. In alkaline conditions, steel or cast iron pipes are sometimes lined with coal-tar enamel or an asphaltic layer over the cement lining for protection.

Materials used for the construction of facilities which cannot be protected with coatings such as valves, small pipes, and pumps include lead, copper, zinc, aluminum, and alloys such as brass, bronze, and stainless steels. Many municipal plumbing codes are not restrictive and a wide variety and mix of material types and installation practices are used for home plumbing. This practice can be conducive to galvanic corrosion. Domestic corrosion can be also be aggravated by the use of home water softening units, inferior grade hot water heaters, and incorrectly sized pipes.

OBJECTIVES

The purpose of this investigation is to collect, review, evaluate, and present existing information to determine whether a sufficient data base is available to develop corrosion control regulations for the water works industry as required by the Safe Drinking Water Act. To accomplish this objective, an exhaustive literature search was completed which included a review of the various materials used in the water works industry and their corrosion characteristics, corrosion monitoring and detection techniques, and corrosion prevention and control strategies. Materials which are addressed are iron-based materials, copper-based materials, lead-based materials, aluminum, asbestos cement, concrete, and plastics. Results of laboratory and field research on each material as related to corrosion in the water works industry are extensively reviewed and data is presented as appropriate. Major emphasis is placed on assessing the conditions of service and water quality characteristics in potable water systems on the corrosion or deterioration of each material.

The review of corrosion monitoring and detection techniques addresses the various methodologies used to identify and evaluate corrosive waters. This discussion includes a review of the search for corrosion indices using water quality monitoring data as well as direct monitoring using coupon exposure tests. The limitations of each of the techniques are presented.

Available corrosion prevention and control techniques are also evaluated and presented. These techniques include adjustments in water quality characteristics, additions of corrosion inhibitors, and the application of various pipe coatings. Additionally, case histories of corrosion control programs are presented for examples.

Finally, the information and data presented in these reviews are compiled and presented in table or matricies form as a summary. These tables provide an overall view of the nature of the corrosion problems in the water works industry and can be used as a data base for the initial consideration of corrosion control regulations.

SECTION 2

CORROSION AND WATER CHEMISTRY BACKGROUND

GENERAL ASPECTS OF CORROSION AND LEACHING IN POTABLE WATER

In general, corrosion refers to the degradation of a metal by electrochemical or chemical reaction with its environment or by physical wearing away. Leaching implies the removal of a soluble constituent, not necessarily metallic, by the action of a percolating liquid. While more often used in relation to ground water systems, leaching has also been used to describe some corrosive dissolutions. This report is concerned with both the physical and chemical degradation of any material used in potable water systems that impart additional species to the water. The nature of corrosion and degradation of materials varies to a large extent with the specific material and environment. Detailed discussions of these interactions with domestic water environments are given in Section 4. These discussions are primarily based on the corrosion and water works literature. Although this literature is voluminous, it is also rather chaotic in the sense that reported results are often not accompanied by sufficient background data or are anecdotal or subject to multiple conclusions. This situation is not surprising in view of the highly complex physical-chemical nature of corrosion processes in general and especially in large-scale field installations. Much of the pertinent literature is oriented to engineering implications of corrosion; there is relatively little information on leaching of constituents of materials with regard to health implications. A number of modes of corrosion or degradation may exist. This report is primarily concerned with those processes which occur on surfaces contacting the potable water and which impart substances to the water. This excludes external corrosion and stress corrosion cracking; the latter is rare in domestic water environments in any case.

The fundamentals of corrosion are given in several textbooks. (See bibliography for this section.) The book by Fontana and Greene is recent and lucid. The text by Butler and Ison has a stronger orientation to corrosion in natural waters and the chemistry of natural waters. The 1948 edition of The Corrosion Handbook by Uhlig compiles a very large amount of data obtained prior to its publication; the more recent work by Uhlig is a useful introductory text. The other references listed are useful for a somewhat different outlook or additional detail on the broad subject of corrosion.

TYPES OF CORROSION

Corrosion types may be classified as either uniform or localized. Uniform corrosion is the loss of a more or less equal amount of material over the surface of a pipe or other structure. It may proceed directly to metal ions which go into solution or by way of a solid reaction product such as metal oxide, hydroxide, carbonate, or other compound. In this case the amount of material imparted to solution may become limited by the solubility of the reaction product compound or by its dissolution kinetics. There is also the possibility of periodic sloughing off of particles or chunks of the reaction product either due to erosion or stresses built up during growth of the layer on the metal. Uniform corrosion is not often a major concern in domestic waters from an engineering or maintenance standpoint. It is a more likely concern from a water quality view since a fairly low uniform corrosion rate, spread over considerable area, can impart more impurity to a given amount of water than a few deep pits.

Localized, or non-uniform, corrosion results in relatively rapid attack and penetration on small areas of metal surface while the remainder of the surface is not affected. Such attack can affect the structural or hydraulic integrity of equipment. Pitting of iron can develop the tuberculation which decreases the flow capacity of pipes. For these reasons, localized corrosion is often an engineering or maintenance consideration. Since attack can be rapid and may result in selective leaching of a metal from an alloy, localized corrosion may also have environmental repercussions. It is noteworthy that either changing to slightly more resistant materials or modifying the parameters in a corrosive medium to reduce the uniform corrosion rate may produce conditions in which localized corrosion is the predominant mode.

Localized corrosion types of interest in potable water systems include pitting, galvanic, concentration-cell, and selective-removal corrosions. Pitting is a general term that refers to the formation of a pit where local anodic conditions exist relative to a nearby cathodic area. Tuberculation occurs when oxides of corrosion products are deposited over or adjacent to the pit. Galvanic corrosion results when two metals of different solution potentials contact each other. The anodic metal will corrode, affording "protection" to the cathodic metal. Concentration-cell corrosion occurs when localized differences in the potential of a single metal exist. Conditions creating this environment could include differences in acidity, cation or anion concentrations, dissolved oxygen, or even temperature fluctuations. Crevice corrosion is a form of concentration-cell corrosion where the rate of oxygen reaching the metal surface is controlled by diffusion in a confined area. Selective-removal corrosion would include dezincification, the removal of zinc from brass, or graphitization, the removal of the iron silicon metal alloy from cast iron, leaving graphite.

CORROSION INDICES

The following presents a brief general discussion of historical attempts to develop a corrosion index. While these indices developed have a potential use, none can be considered as a single tool for formulating a responsible corrosion control program.

In 1912, J. Tillmans proposed the carbonate saturation theory of pipe protection. Since then, several theoretical and empirical approaches have been made to determine a single parameter that would indicate the ability of a given water to protect or corrode the carrying pipes.

In 1936, W. F. Langelier developed the Langelier Saturation Index (9). The SI is based on the theoretical tendency of a water to deposit or dissolve calcium carbonate. The index is derived from the solubility product of calcium carbonate, the dissociation constant of water, the second dissociation constant of carbonic acid ($H^+ + CO_3^= \rightleftarrows HCO_3^-$), and a stoichiometric equilibrium between alkalinity and protons versus the carbonate, bicarbonate, and hydroxyl species. By restricting the applicable pH to 6.5-9.5, a saturation pH, pH_s, is determined as:

$$pH_s = (pK_2' - pK_s') + pCa + pAlk$$

where $pX = \log(\frac{1}{X})$ and

Ca = calcium ion concentration in moles/liter

Alk = total alkalinity as equivalents/liter

K_2' = second dissociation constant of H_2CO_3, corrected for ionic strength and temperature

K_s' = solubility product of $CaCO_3$, corrected for ionic strength and temperature

The saturation index is: $SI = pH - pH_s$.

It is a logarithm of the ratio of the hydrogen ion concentration that the water must have if saturated with calcium carbonate to the actual hydrogen ion concentration. A negative value indicates an undersaturation of $CaCO_3$ and, hence, a tendency to dissolve any existing $CaCO_3$ coating. A positive value indicates oversaturation, a tendency to precipitate $CaCO_3$ and to form a protective layer.

Correlation attempts between the calculated SI and observed corrosion effects have often, but not always, been in agreement. In general, a corrosion free system exists when the SI is greater than -0.5 for cold water and 0.0 for hot water, provided the water is of moderate hardness and alkalinity (7), where the Langelier presumption of calcite being the $CaCO_3$ phase is less apt to be discrepant from impure calcite or precipitation inhibition. The SI is similarly not suitable for use in soft, saline waters where a low buffer capacity and ionic species such as chlorides may disrupt the $CaCO_3$ equilibrium conditions. Parameters that must be evaluated to calculate the SI are methyl orange alkalinity, pH, temperature, total dissolved solids, and the calcium ion concentration.

When using the SI, it is imperative to remember that this parameter states a difference between actual pH and a pH at which $CaCO_3$ equilibrium is theoretically achieved for that water. It says nothing about the driving force or tendency for the $CaCO_3$ to dissolve or crystallize in the given water. Differences may result from temperature effects, specific uncharged or ionic constituents in the water, or crystal growth inhibition. Increased temperatures will decrease the solubility of calcium carbonate as well as increase reaction velocities, and consequently establish local equilibrium situations much faster than at normal temperatures. There may also exist a difference in pH between the $CaCO_3$ saturation point and the point at which crystal growth actually begins. This difference, called the metastable region, may increase in the presence of other dissolved ions, especially those that form slightly soluble salts with calcium or carbonates such as magnesium or sulfate, causing a poor correlation between the calculated SI and actual conditions of solubility.

A commonly used refinement of the SI that includes temperature and ionic strength corrections is

$$pH_s = A + B - \text{Log}\ (Ca^{++}) - \log\ (\text{alkalinity})$$

where A and B are constants derived from the following tables:

Water Temperature C	A	mg/l Total Filterable Residue	B
0	2.60	0	9.70
4	2.50	100	9.77
8	2.40	200	9.83
12	2.30	400	9.86
16	2.20	800	9.89
20	2.10	1,000	9.90
25	2.00		
30	1.90		
40	1.70		
50	1.55		
60	1.40		
70	1.25		
80	1.15		

TABLE 1. Correction Parameters Used With The Refined SI

Other corrosion indicators include the Ryznar, Larson, Driving Force, Casil, Aggressive, and Riddick indices. The Ryznar Stability Index is defined as

$$RI = 2pH_s - pH$$

with pH_s and pH defined as before. A value of seven or greater indicates an aggressive water while 6 or less indicates a tendency to form scale (17). This index may be used with moderate to hard waters, but is not applicable to soft or saline waters for the reasons previously cited.

The Larson index attempts to measure the aggressive nature of specific ions and is defined as:

$$LI = \frac{Cl + SO_4}{Alk}$$

where Cl and SO_4 are the chloride or halogen concentrations and sulfate concentrations, repectively, and Alk is total alkalinity. All three are expressed in mg/l of equivalent $CaCO_3$. When this ratio of reactive anions to alkalinity is greater than 0.5, the possibility of corrosive action exists. Unlike the SI, this index does not refer to the solubility of $CaCO_3$ but rather to the faster rates of corrosion of metals because of conductivity effects. It is not applicable to water that is soft or has a low dissolved solids concentration.

The driving force index is defined as:

$$DFI = (Ca^{++}) \times (CO_3^{=})/K_s' \times 10^{10}$$

$$DFI = 10^{SI}$$

where the calcium and carbonate concentrations are expressed in mg/l as $CaCO_3$, and K_s' is the $CaCO_3$ solubility product, corrected for ionic strength and temperature. This index is a ratio of the actual ion product to that which would exist during equilibrium conditions. Values greater than 1.0 indicate a tendency for deposition of $CaCO_3$ while values lower than 1.0 indicate a $CaCO_3$ dissolution condition.

The Casil Index is a modification to the calcium carbonate solubility indices that accounts for the effect of other parameters for soft waters. It is defined as

$$CI = Ca + Mg + HSiO_3 - \frac{Anions}{2}$$

where each concentration is expressed in milliequivalents per liter. Negative values are considered indicators of very corrosive water, values between 0 and 0.1 indicate slightly corrosive waters, and values above 0.1 indicate noncorrosive conditions.

The aggressive index was formulated to determine the quality of water that can be transported through asbestos-cement pipe without adverse structural effects. It, however, does not incorporate temperature or TDS effects nor does it indicate the tendency of the pipe to release fibers or allow $Ca(OH)_2$ leaching.

Aggressive Index = pH + log (AH) where

A = total alkalinity as mg/l $CaCO_3$

H = calcium hardness as mg/l $CaCO_3$

According to the AI, values greater than 12 define a nonaggressive water; values less than 10 define a highly aggressive water; and values between 10 and 12 define a moderately aggressive water.

The Riddick Corrosion Index is an empirically based formula that weighted several corrosion-influencing factors including dissolved oxygen, chloride ion concentration, noncarbonate hardness, and silica. The Riddick Index is

$$RCI = \frac{75}{Alk} \left[CO_2 + \frac{1}{2}(Hardness - Alk) + Cl^- + 2N\right] \left(\frac{10}{SiO_2}\right) \left(\frac{D.O. + 2}{Sat.D.O.}\right) (12)$$

where CO_2 is expressed as mg/l $CaCO_3$
Hardness is expressed as mg/l $CaCO_3$
Cl^- is the chloride ion concentration as mg/l
N is the nitrate ion concentration as mg/l
D.O. is the dissolved oxygen as mg/l
Sat.D.O. is the saturated oxygen value as mg/l.

The results are interpreted as

0 - 5	extremely noncorrosive
6 - 25	noncorrosive
26 - 50	moderately corrosive
51 - 75	corrosive
76 -100	very corrosive
> 100	extremely corrosive.

The values obtained correlated well with the soft waters in the eastern part of the U.S., but not to the harder waters found in the middle states.

A more recent attempt to index the corrosivity of waters resulted from a combination of the ratio:

$$\frac{(Ca^{++})\ (HCO^-)^2}{(CO_2)}$$

which represents the $CaCO_3$ precipitation equilibrium in the reaction:

$$Ca^{++} + 2HCO_3^{=} \rightleftharpoons CaCO_3(s) + CO_2(g) + H_2O$$

and the Larson Index. When corrected for low hardness cases, the result is:

$$Y = AH + B[Cl^-] + [SO_4^{=}]\ \exp(-\frac{1}{AH}) + C$$

where $A = 3.5 \times 10^{-4}$
$B = 0.34$
$C = 19.0$
$H = \frac{(Ca^{++})\ (HCO_3^-)^2}{(CO_2)}$

$[Cl^-]$, $[SO_4^{=}]$, $[Ca^{++}]$, $[CO_2]$ are expressed in ppm

$[HCO_3^-]$ is expressed in ppm as $CaCO_3$

A correlation between this index and the scale formed by waters of that constituency is shown in Table 7. The scale was quantified by impedance measurements and only three samples were analyzed. However if substantiated, this index would indicate that the chloride and sulfate concentrations, while conventionally regarded as corrosive factors, may actually assist in the crystal growth of calcium carbonate and resultant pipe protection.

A summation of the indices is presented below.

TABLE 2. CORROSION INDICES

(numbers in parenthesis refer to corrosion indices bibliography, symbols are explained in the test)

Langelier Saturation Index (9, 10)

$$S.I. = pH - \{(pK_2' - pK_s') + pCa + pAlk\}$$

Ryznar Stability Index (17)

$$R.I. = 2pH_s - pH$$

Larson Index (11, 12)

$$L.I. = \frac{Cl + SO_4}{Alk}$$

Driving Force Index (14)

$$DFI = (Ca^{++}) \times (CO_3^{=})/K_s' \times 10^{10}$$

Casil Index (13)

$$C.I. = Ca + Mg + HSiO_3 - \frac{Anions}{2}$$

Aggressive Index (15)

$$A.I. = pH + Log[AH]$$

Riddick Corrosion Index (16)

$$R.C.I. = \frac{75}{Alk}\left[CO_2 + \frac{1}{2}(Hardness - Alk) + Cl + 2N\right]\left(\frac{10}{SiO_2}\right)\left(\frac{D.O. + 2}{Sat.D.O.}\right)(12)$$

Feigenbaum, Gal-or, Yahalom combination (8)

$$Y = AH + B([Cl^-] + [SO_4^{=}])\exp\left(-\frac{1}{AH}\right) + C$$

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SECTION 3

MATERIALS USED IN THE WATER WORKS INDUSTRY

A variety of materials are used by the water works industry for the construction of facilities for treatment, storage, and distribution of potable water supplies. The majority of materials are used for pipes and piping and for water storage or pressure tanks. For many small installations, no treatment facilities exist and the water utility facilities consist of only pumps, pipelines, and storage/pressure tanks.

The various materials used by the water works industry are identified and briefly described in this section. Emphasis is placed on those materials used for pipes and piping and for water storage as any corrosion control regulations or utility programs will be primarily governed by the performance of these facilities and materials. Materials used for the construction of water treatment facilities are essentially the same as those used for pipelines and storage tanks and, therefore, are not neglected from this presentation.

PIPES AND PIPING

Pipes used in the water works industry are categorized under four classifications, excluding household plumbing. These four classifications are transmission lines, distribution mains, service lines, and in-plant systems.

Transmission lines are those pipes used to transport water from the water resource to the treatment facilities or finished water from the treatment facilities to a community distribution system. These pipes can be significantly large and occasionally a tunnel is required if the maximum size pipe available is insufficient for design. Transmission lines are usually designed for gravity flow to avoid pumping costs and to reduce line pressures. Design flow velocities should not exceed 5 fps, but sometimes range from 12 to 15 fps. Factors which should be considered when selecting a particular material for a transmission line are corrosion resistance, structural qualities, hydraulic characteristics, installation and field conditions, and economics.

Distribution systems are those facilities used to carry water from the transmission lines and distribute it throughout a community. The distribution system includes a network of pipelines or mains, distribution reservoirs, elevated storage tanks, booster stations, and valves. Components of the distribution system include arterial mains, distribution mains, and a valve system. Arterial mains, sometimes called trunk mains or feeders, are used to connect transmission lines to the distribution lines. Arterials are normally placed in a loop arrangement to avoid dead ends. Distribution lines are connected to the arterial loop forming a grid system. These lines are used to serve communities or commercial areas and hook up to individual service lines.

Materials commonly used for transmission lines and distribution mains are asbestos cement, cast iron and ductile iron, concrete, plastic, steel, and wrought iron (2). The advantages and disadvantages of the use of these materials are presented in Table 3. Aluminum is also used for pipelines, but to a lesser extent (1). Plastic and wrought iron are more commonly used in service lines and in-house plumbing systems (4).

Service lines are small diameter pipes that connect the consumer to the distribution main. The selection of a particular material for a service line is influenced by required size, durability, water characteristics, corrosion resistance, material availability, ease of installation, and economics. These criteria as well as corrosive tendencies of the waters in the specific area are usually reflected in the local plumbing codes. Because of its excellent physical characteristics, lead was the earliest material used for service lines. However, the use of lead is now being questioned because of its cost and its tendency to dissolve in soft waters of low pH. Copper is now more frequently selected for service lines and approximately 50 percent of the water utilities in the U.S. use copper exclusively. However, plastic pipe is becoming more popular (4).

Minimum size service lines range from 3/4 to 1.0 inches in diameter. For larger residences with numerous baths, minimum size service lines will range from 1-1/4 to 1-1/2 inches in diameter. Approximately one-half of all service lines in the U.S. are owned by utilities and the other one-half are owned by the customers. However, approximately two-thirds of all service lines are installed by utilities (4).

The most commonly used piping materials for service lines are asbestos cement, brass, cast iron, copper, galvanized iron, lead, plastics, steel, and wrought iron. The hydraulic flow characteristic of all these piping materials is good when initially installed. These flow characterictics generally remain good for asbestos cement, copper, lead, and plastic. These materials are listed and briefly characterized in Table 4.

Flexible materials used for service lines are usually connected directly to the corporation cock on the main and to the stop valve within the household. Nonflexible materials require the use of a "gooseneck" connection to the corporation cock and possibly some type of flexible connection to the household plumbing system. Goosenecks are available in lead, copper (if permitted by local plumbing codes), and flexible plastic (4).

Every type of piping material previously discussed is used for in-plant piping systems. Other materials used include glass and rubber. Glass and rubber are not usually used for conveying potable water within the plant, but rather for other in-plant operational functions. Pipe materials used for

TABLE 3. SEVERAL MATERIALS USED FOR TRANSMISSION AND DISTRIBUTION LINES (4)

Materials	Available Size Diam. (in.)	Advantages	Disadvantages
Asbestos Cement	4-36	Corrosion resistant; good flow characteristics; light weight; easy handling; low maintenance.	Low flexural strength in small sizes; more subject to impact damage; difficult to locate underground.
Cast Iron (cement-lined)	2-48	Durable and strong; good corrosion resistance; easily tapped; flow characteristics good.	Subject to electrolysis and attack from acid and alkaline soils; heavy to handle.
Ductile Iron (cement-lined)	4-54	Durable, strong, high flexural strength; lighter weight than cast iron; greater carrying capacity for same external diameter; fracture resistant; easily tapped.	Similar to cast iron.
Concrete (reinforced)	12-168	Durable with low maintenance; good corrosion resistance; flow characteristics good; resists backfill and external loads.	May deteriorate in alkaline soil, if cement type is improper, or in acid soil if not protected.
Concrete (prestressed)	16-120	Durable, low maintenance; good corrosion resistance; good flow characteristics; resists backfill and external loads.	Same as above.

(Continued)

TABLE 3 (Continued)

Materials	Available Size Diam. (in.)	Advantages	Disadvantages
Steel	4-120	Light weight and easily installed; high tensile strength; low cost; good hydraulically when lined; adapted to locations where some movement may occur.	Subject to electrolysis; external corrosion in acid or alkaline soil; poor corrision resistance unless properly lined, coated, and wrapped; low resistance to external pressure in larger sizes; air-vacuum valves imperative for large sizes; subject to tuberculation when unlined.
Plastics			
ABS PE PVC	1/2-12 1/2-6 1/2-16	Smooth interior surface minimizes pumping losses; chemically inert; corrosion resistant, non-reactive with water; light weight.	Jointing sometimes difficult; tendency to creep; brittle at low temperatures.
Wrought Iron	1/4-30	Tough; ductile; malleable; weldable and corrosion resistant.	Generally rough surface; hot dip galvanizing or non-metallic coating generally required.

TABLE 4. MATERIALS USED FOR SERVICE LINES (4)

Material	Size range (in.)	Comments
Asbestos-Cement	3,4,6	Corrosion resistant; not available below 3-in.; slip coupling joints.
Brass	1/2 to 6	Long life under normal conditions; corrodes in acid soils; uses threaded coupling joints; requires gooseneck connection.
Cast iron	2,3,4,6	Corrosion resistant when lined and coated; not available in small diameters; rigidity and short length require joints and gooseneck connection.
Copper	1/2 to 6	Direct connection to mains; corrosion resistant; dissolves in soft water with high CO_2 content.
Galvanized iron	1/2 to 3	Not highly resistant to corrosion; requires threaded joints and gooseneck connection.
Lead	3/8 to 2	Direct connection mains; corrosion resistant except in soft waters with high CO_2; some tendency to creep or crack unless properly formulated.
Plastics		
ABS	1/2 to 6	
PE	1/2 to 2	
PVC	1/2 to 6	
Steel	1/2 to 6	Available in three grades; strong, extra-strong, double extra-strong; not resistant to corrosion unless cement-lined.
Wrought iron	1/2 to 6	Same comments apply as for steel.

in-plant systems for transporting potable waters have the same design and are manufactured by the same process as previously discussed.

The extent of use of various materials for piping by water utilities serving more than 2500 persons in the U.S. as of 1975 and for 1975 was surveyed and compiled by Scott and Caesar and is summarized in Table 5 (3). Approximately 75 percent of all water main piping in the U.S. as of 1975 was cast iron and it accounted for approximately 46 percent of total pipe installed in 1975. Asbestos cement pipe and steel pipe accounted for approximately 13 and 6 percent, respectively, of all water mains in place by 1975. The use of steel pipe appears to be declining as it accounted for only approximately 3.4 percent of all water pipes installed in 1975.

STORAGE TANKS

Materials used for the construction of water storage tanks are wood, fiberglass, concrete, and steel. Aluminum is sometimes used for construction of storage tank roofs. The type of material selected is generally determined by the required capacity, the specific use, and economics. Concrete is considered economical for large storage tanks with capacities ranging between 1.25 and 5 million gallons. Concrete tanks are estimated to constitute 15 percent of all new water tanks (2).

Steel tanks are considered more economical for tank capacities smaller than 1.25 million gallons, and they are more adaptable for elevated use when natural relief or topography is not available (2). However, steel tanks are often lined with a protective coating, such as a coal tar, to minimize corrosion. Consequently, the maintenance costs of steel tanks is generally higher than that for concrete tanks (2).

Currently there are approximately one-half million steel water storage tanks in the U.S. ranging in capacity from 50,000 gallons to 10 million gallons. It is estimated that over 1000 new steel water tanks are constructed each year (2).

Wooden tanks generally have capacities ranging in size from 25,000 to 50,000 gallons, but can be as large as 250,000 gallons. Because these tanks have limited capacities and are prone to leak, their use is limited (2).

Fiberglass-reinforced plastic tanks are also used for storage of potable water, but to a limited extent owing to problems encountered in field construction. Because of these construction problems, most of these tanks are limited in capacity to that which can be shop fabricated and transported. Fiberglass tanks have been shop fabricated up to capacities of nearly 50,000 gallons (2).

Steel storage tanks are usually lined with a water-impervious coating. Traditionally, these coatings have been coal tar based enamels, but recent difficulties in controlling fumes during application and reports that toxic

TABLE 5. PIPE USED IN U.S. WATER SUPPLY DISTRIBUTION SYSTEMS BY UTILITIES SERVING OVER 2,500 PERSONS (3)

TYPE OF PIPE	MILEAGE IN PLACE (beginning of 1975)	% OF TOTAL	MILEAGE INSTALLED (1975)	PERCENT OF PIPE MILEAGE IN PLACE AT BEGINNING OF 1975 BY DIAMETER			
				Under 6"	6"-12"	13"-24"	Over 24"
Cast Iron	481,816	75.29	6,847	15.7	76.7	6.6	1.0
Asbestos Cement	83,871	13.11	3,743	9.7	86.3	4.0	0.1
Steel	37,852	5.91	505	53.4	29.5	10.7	6.4
Reinforced Concrete	10,083	1.58	517	0.2	4.1	43.4	52.3
Plastic	6,981	1.09	1,826	62.0	37.3	0.6	0.1
Ductile	7,498	1.17	1,388	*	*	*	*
Galvanized Wrought Iron	2,364	0.37	3	*	*	*	*
Wood	1,246	0.19	*	*	*	*	*
RCP Steel Cylinder	652	0.10	8	*	*	*	*
Black Galvanized Iron	431	0.07	*	*	*	*	*
Copper	312	0.05	*	*	*	*	*
All others and unidentified	6,879	1.07	96				

Source: Scott and Caesar, 1975 (3)

*Not Specified

substances may be introduced to the waters by their use have resulted in the use of epoxy and vinyl paints (2). Various estimates report that 50-90% of all new water tanks are lined with vinyl and 10-50% are lined with epoxy (2).

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SECTION 4

CORROSION CHARACTERISTICS OF MATERIALS USED IN THE WATER WORKS INDUSTRY

The corrosive behavior of specific materials when subject to the environmental conditions of potable water systems is presented in this section. This information is compiled primarily from published results of laboratory and field research. In general, most studies reviewed are consistent and in agreement in identifying the conditions of service and water quality characteristics which initiate and maintain the corrosion or deterioration of a specific material. However, specific data presented by various investigators is sometimes inconsistent or in disagreement. This inconsistency usually results from variations in the conditions of testing and/or reporting. It is also noted that the literature often fails to fully describe or present the details of the testing procedures which are often critical for assessing test results.

The corrosion behavior of each material is discussed independently and the presentation format for each material is dictated by the information available in the literature. Emphasis is placed on presenting numerical results of various corrosion testing and monitoring as this data serves as the basis for considering specific corrosion control alternatives.

IRON-BASED MATERIALS

Iron-based materials are among the most common piping materials. They are also subject to a variety of corrosion mechanisms that may occur in potable water systems. This subsection discusses the various iron-bearing metals that may be encountered.

Corrosion of Iron

The corrosion behavior of steel and cast iron materials in potable water environments is highly complex. Many factors can be involved and are often interrelated. The effects of several factors can vary from beneficial to conducive to greater corrosion, depending on the specific situation. It is often difficult to say what the main factor controlling the corrosion of steel is, due to these subtle relationships. The following discussion outlines the basic corrosion mechanism of iron and then discusses these contributing factors.

The corrosion of iron and steel in waters is basically electrochemical in nature. The actual metal loss is due to an oxidation of iron atoms on the metal surface to give ferrous ions which can go into solution and electrons which stay with the metal:

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (1)$$

In order for this process to proceed, the electrons must be taken up by a reduction process which can take place on another part of the surface. Usually this complementary process is the reduction of dissolved oxygen (Eq. 2) or the reduction of hydrogen ions or related species (Eq. 3).

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (2)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (3)$$

The oxidation and reduction reactions are parallel-coupled events which must proceed at identical rates. The overall corrosion rate is limited by the slower of the two coupled reactions. The oxidation reaction (Eq. 1) is rapid in most media. The rates of the reduction reactions are limited in natural waters by reactant concentrations, sluggish electrochemical kinetics, or a combination of factors. Thus the overall uniform corrosion rate is normally controlled by the rate of the reduction reaction, as amplified below.

For corrosion to occur, the difference between the electrochemical potentials for the oxidation reaction (occurring at anodic sites) and reduction reactions (occurring at cathodic sites) must be such that the overall free energy change drives the reactions as written. This potential difference ultimately appears as a driving force which can be viewed as being divided between the two reactions in such a way that the inherently slower reaction receives the larger share of driving force. For iron corrosion with hydrogen ion or water reduction, this overall driving force is relatively small and decreases with increasing pH. On the other hand, the driving force for iron corrosion with oxygen reduction is very large. The reduction of oxygen is a complex electrode process which is inherently quite slow. The detailed mechanism is not well known. In spite of the low inherent rate, the driving force is so large that the reduction can be fast, and transport of O_2 to the iron surface often becomes the rate limiting process.

The metal loss will be uniform or general over the surface as long as the oxidation and reduction sites constantly shift in location and the fractional coverage of sites is roughly the same. If an oxidation site becomes small, fixed, and surrounded by a much larger reduction area, then localized corrosion such as crevice corrosion or pitting can result. This localization of an oxidation site can be caused by a variety of factors such as local breakdown of a protective oxide film, presence of a crevice, a break in a deposit on the metal, and so on. Uniform corrosion is favored by a clean metal surface and ample supply of cathodic reactant. Thus in acidic solutions where oxide films are not stable and the concentration of hydrogen ions is high, steel generally corrodes uniformly. Localized corrosion is often favored by conditions which reduce the rate of uniform corrosion. Factors influencing the type of corrosion are also related to the effects of oxygen concentration, pH, flow rate, temperature and electrolyte concentration, which in turn do not operate independently. These factors are taken up separately below, but their interdependence should be kept in mind.

It is tempting to attribute a majority of the factors involved in corrosion of iron in aerated near neutral pH waters to control by oxygen transport (cathodic control). Stumm strongly suggests, however, that at long exposure duration, formation of protective films on iron and other events may make the rate of the anodic iron dissolution process an important factor (97). Although cathodic control appears to explain a large number of environmental effects, the latter possibility should also be kept under consideration.

Effect of Dissolved Oxygen--

Dissolved oxygen plays a key role in corrosion or iron in natural waters, but its effects can be conflicting and partially dependent on other environmental factors. In near neutral pH waters at ambient temperature, dissolved oxygen provides the reduction reaction (Eq. 2) which sustains the corrosion of iron. However, oxygen also plays a role in formation of semi-protective iron oxide films on the metal, and the more protective films are formed at higher oxygen concentrations. The presence of oxygen also appears to be necessary for formation of protective layers on steel by calcium carbonate deposition (7). Once these films are formed, however, oxygen provides the main driving force for initiation of pitting (leading to tuberculation) or other forms of localized corrosion.

The first part of this discussion is for conditions in the absence of calcium carbonate or other external inhibiting species. At sufficiently high pH values, iron oxide or hydroxide layers can be formed. The first of these is probably ferrous hydroxide which can be formed by an overall reaction such as Eq. 4.

$$Fe + H_2O + 1/2\ O_2 \rightarrow Fe(OH)_2 \qquad (4)$$

This solid is often found next to the metal surface and can act as a diffusion barrier to oxygen. Further oxidation of this product yields hydrous ferric oxide which comprises most of ordinary rust. An intermediate oxidation stage, $Fe_3O_4 \cdot nH_2O$ often forms as a layer between the ferric and ferrous compounds.

In the absence of dissolved oxygen, the corrosion rates for both pure iron and steel becomes negligible in near neutral pH water at room temperature. Corrosion rates may be high when the metal is first exposed to air-saturated water, but the iron oxide films formed over a period of a few days act as a barrier to diffusion of oxygen to the surface and a steady state corrosion rate is obtained. This steady state rate is proportional to oxygen concentration, as shown in Figure 1,since the oxygen diffusion rate is proportional to its concentration. An oxygen concentration of about 6 mg/l corresponds to air-saturated water. At still higher oxygen concentrations, the uniform corrosion rate of mild steel may decrease abruptly, as shown in Figure 2. This effect is apparently due to passivation of the iron which involves either the oxidation of the normal ferrous hydroxide layer to one which has better protective properties or the formation of a thin chemisorbed oxygen layer on the metal surface. More oxygen is required in waters

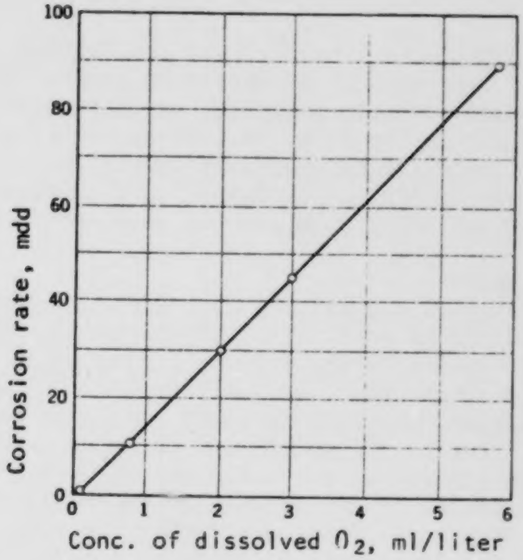


Figure 1. Effect of O_2 concentration on corrosion of mild steel in slowly moving water containing 165 ppm $CaCl_2$, 48-hour test, 25°C (107).

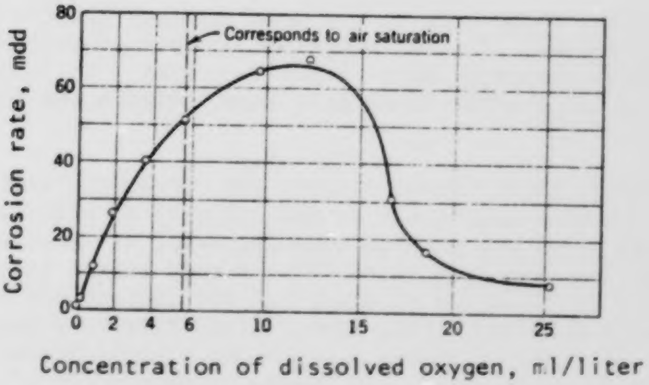


Figure 2. Effect of O_2 concentration on corrosion of mild steel in slowly moving distilled water, 48-hour test, 25°C (107).

containing chloride ions and passivation of mild steel connot occur if the chloride concentration is high enough. The breakdown of passivity in the presence of moderate amounts of chlorides (more than about 20 ppm, see below) is often accompanied by severe pitting or crevice corrosion.

The effect of solution flow rate on mass transport of oxygen to the corroding surface can also give rise to diverse effects. At moderate oxygen concentrations and flow rates, increasing the flow rate increases the corrosion rate due to the increase in amount of oxygen transported to the surface. At higher flow rates, the surface oxygen concentration can become high enough to cause passivation, provided the chloride content is not too high. These effects are shown in Figure 3. Still higher flow rates, over 15 ft/sec, can greatly accelerate corrosion by erosion of the protective films, combined with fast transport of oxygen to the surface by turbulent flow. At the other extreme, stagnant conditions are usually most conducive to pitting and other forms of localized corrosion. The threshhold for chloride effects on passivity is ill defined. As little as 20 ppm chloride may cause breakdown and pitting but the threshhold may be higher depending on solution composition (vida infra).

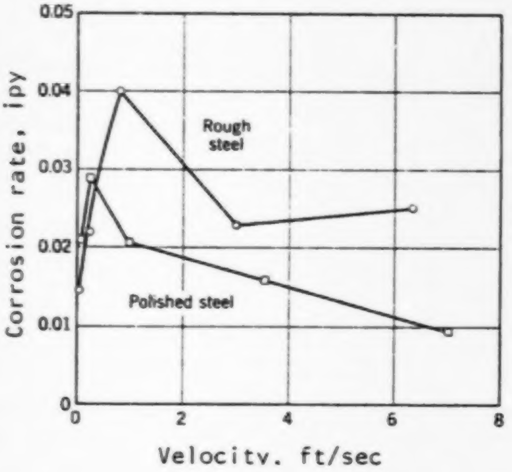


Figure 3. Effect of velocity on corrosion of mild steel tubes containing Cambridge water, 21°C, 48-hour tests (87).

Effect of pH--

Conflicting results and conclusions have been obtained for the effect of pH on corrosion of steel and cast iron in potable water environments. This is probably because a number of effects are possible in the range of interest, from about pH 6 to pH 10, and both the mode of corrosion as well as degree of corrosion and structure of surface films may be affected. In addition, all attempted correlations are done with respect to the bulk pH of the liquid phase, while the actual pH at the material surface can be affected by the corrosion reactions, surface iron hydroxide layers, other precipitated layers, other chemical species in solution, and solution flow rate.

In the moderately acidic region, corrosion is generally uniform and the rate increases rapidly with decreasing pH. The onset of this region is about pH 4 to 5 if no other acidic species other than hydrogen ions are present, and from about pH 5 to 6 if acidic species such as dissolved carbon dioxide are present in appreciable quantities. Corrosion is accelerated in these regions because hydrogen evolution can occur utilizing fairly concentrated reagents (hydrogen ions or protonated anions). In addition, the oxide films which act as diffusion barriers are dissolved. The latter effect also offers greater access of oxygen to the metal surface which can be more important than hydrogen evolution at the higher pH end of this range. Both hydrogen evolution and oxygen reduction tend to raise the pH at the metal surface and stabilize oxide films. The presence of acidic species such as dissolved CO_2 tends to mitigate this effect since the total acidity of such a system is greater than that of a completely dissociated acid at the same pH.

In the near neutral pH range of most natural waters, oxygen transport can in some cases dominate changes in pH, although in this region many complex pH effects have been noted. The simplest type of behavior for corrosion of steel by aerated water at 22°C is shown in Figure 4 (112). For this case, in which either NaOH or HCl were added to aerated water to adjust the pH, the corrosion rate is constant from about pH 4 to 10. This is reasonable behavior if the rate depends only on diffusion of oxygen to the metal surface through a diffusion barrier of ferrous hydroxide or hydrated ferrous oxide which is continuously renewed by the corrosion process. Also, in this bulk solution pH region, the iron surface is always in contact with the saturated ferrous hydroxide solution which should maintain a pH of about 9.5. Similar results were obtained at 40°C except the constant corrosion rate plateau (18 mpy) extends from pH 4.5 to 8.5. When the pH is adjusted with CO_2 instead of HCl, the rapid increase in corrosion rate occurs at pH 5.4 instead of 4.1 (112).

Later studies have occasionally shown a maximum in corrosion rate occurring in the pH range from about 6 to 9. Examples are given by Eliassen, et al, along with controlled corrosion tests using synthetic "average" water (84 ppm hardness, 57 ppm methyl orange alkalinity, and a pH after aeration of 8.05, pH_s = 8.28) (25). These tests were done for steel pipe as a function of flow rate and duration of exposure. A maximum in the corrosion rates was observed in the pH range 6.5 to 7.5 for short-term tests (7-14 days exposure) at flow velocities of 0.33 and 1.0 fps. At zero velocity a much lower corrosion rate was observed which was constant from pH 4 to 11. The authors note that their short-term results are quite similar to others in the literature which show corrosion maxima with pH (25). However, their "long-term" tests (30-40 days) do not show maxima and tend to agree with the early results of Whitman (112). These results are illustrated in Figure 5. These authors also observed very severe pitting at a pH of 6.5, slight pitting at pH 8.0 to 10.0 and no pitting at pH 4.0 to 5.5. They generally agree with the model of pH effects proposed by Whitman, but point out that variations may be caused by changes in mode of corrosion and nature of corrosion products formed as a

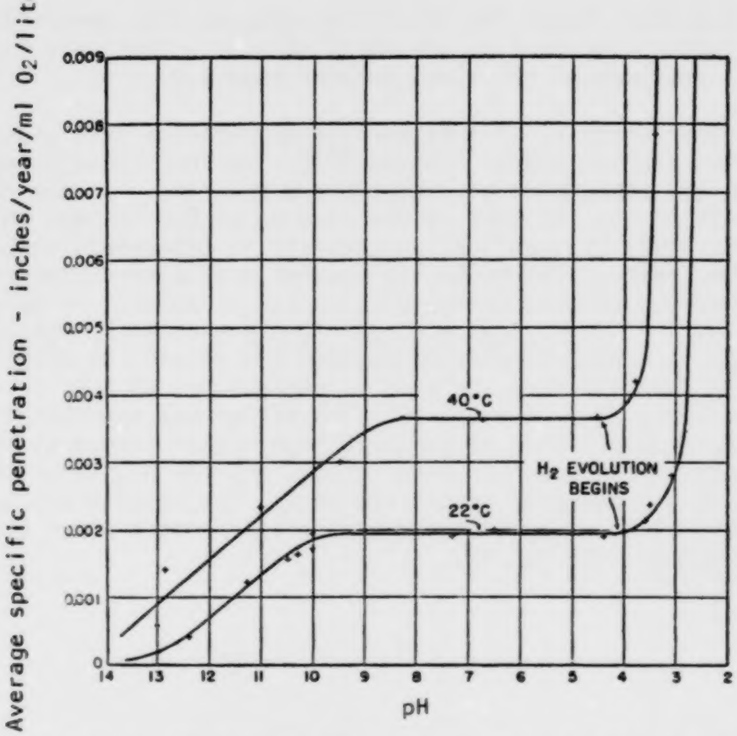


Figure 4. Effect of pH on corrosion of mild steel (112).

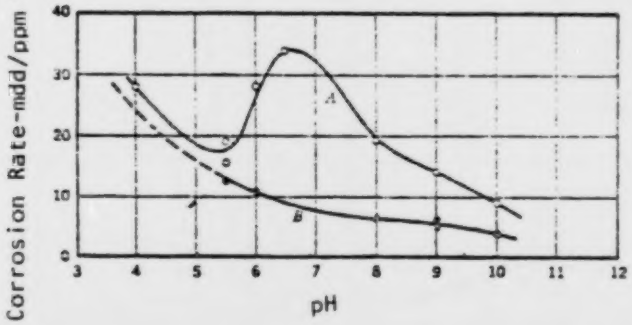


Figure 5. Effects of test duration on pH-corrosion relationship (25).
A. 7-14 day tests.
B. 30-40 day period.

function of pH and also time. The corrosion products they observed were gelatinous and loosely attached to the metal in acid waters, but hard, raised, and well attached at pH values greater than 8.0.

Some additional examples of more complex pH behavior have been given by Larson (57, 59, and 60) and by Fontana (32). Larson's results were obtained with waters containing bicarbonate and chloride. In one case, at a Cl^-/alk mole ratio of 0.4, a sharp maxima at a pH of 8.0 is seen which increases with duration of exposure, in contrast to Eliassen's results (60). These results are shown in Figure 6. In another case with a higher chloride content, the corrosion rates increase by a factor of about 3 in going from pH 7 to pH 8.5 (at a Cl^-/alk ratio of 1.0). Fontana obtained results for a sample maintained in a high flow rate location (39 ft/sec) in distilled water at 50°C. A sharp peak in corrosion rate is observed at pH 8 which is about 10 times that observed at pH 6 or pH 10. The effect was attributed to an atypical reaction product scale of granular Fe_3O_4 which formed at pH 8. In regions of low attack the products were $Fe(OH)_2$ and $Fe(OH)_3$ which provided better barriers to diffusion of oxygen and ions. The results are said to be supported by power plant experience showing greater attack at pH 8 as compared to slightly lower values (32).

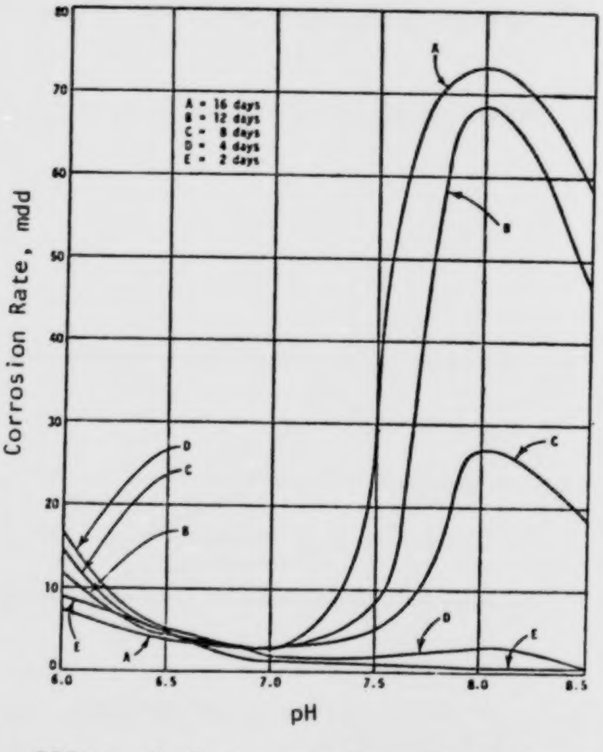


Figure 6. Effect of pH on corrosion rate at chloride-alkalinity ratio of 0.4; duration: A, 16 days; B, 12 days; C, 8 days; D, 4 days; E. 2 days (60).

An increase in corrosion rate with increasing pH (from pH 6.9 to 8.6) has also been reported for ground cast iron samples in a variety of natural and synthetic waters after 50 days exposure (97). The author attributes this to a decrease in buffer capacity of the electrolyte (for a given alkalinity) with increasing pH and to the pH dependence of relative local anode/cathode areas. These views are discussed in the calcium carbonate protection section below.

Some relatively recent electrochemical results may give additional insight on the pH behavior. The fundamental corrosion reactions on iron have been mainly studied in deaerated solutions at a pH less than 5 under conditions where no solid reaction products are formed. The oxidation reaction (Eq. 1) appears to proceed through intermediates involving hydroxyl ions in such a way that its individual rate increases with increasing pH from about pH 1 to pH 5 (46). Hydroxyl ion catalysis at near neutral pH might help explain the disparate experimental results in natural waters.

Effect of Dissolved Salts--

Dissolved salts (for example, ions such as Na^+, Cl^-, $SO_4^=$, Ca^{++}, Mg^{++}, HCO_3^-, $CO_3^=$, etc.) can have a number of effects, some of which depend only on the general effect of ions, while others depend on the individual chemical species. Examples of the first class of effects are given below.

- Increasing salt concentration increases solution conductivity which can have several effects.
- Increasing salt concentration generally decreases the equilibrium concentration of dissolved oxygen and CO_2.

Contrary to early predilections, solution conductivity itself has little effect on most modes of uniform or localized corrosion. This is because the local anodes and cathodes are so close together that the resistance offered by the solution is much less than equivalent electrochemical reaction rate resistances. Solution conductivity can, however, affect the range over which the effects of attack due to galvanic coupling of dissimilar metals is extended. Attack can extend for example, from about 1 cm from the joint in soft waters to more than 10 cm in water with significant dissolved salt content. Galvanic corrosion is discussed in a later section.

Changes in solution conductivity can have more subtle and significant effects. Uhlig proposes that moderate increases in conductivity (by dissolved NaCl) from that of very soft or distilled water can lead to increased corrosion rates due to formation of a less protective $Fe(OH)_2$ film (107). The corrosion of iron in aerated solution as a function of NaCl concentration is shown in Figure 7. The film is less protective since it is formed further away from the surface than in less conductive waters. This in turn is due to coupling of local anodic (source of Fe^{2+}) and cathodic (source of OH^-) areas at greater distances in the more conductive solution. The initial increase in corrosion rate might also have to do with some specific effects of chloride and a number of postulates on these effects have been offered (31).

Specific effects of chloride are discussed below. There is little direct evidence for either the $Fe(OH)_2$ film or chloride effect arguments.

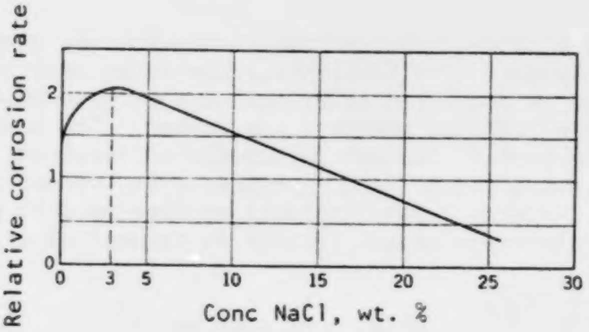


Figure 7. Effect of NaCl concentration on corrosion of iron in aerated solutions, room temperature (107).

It has recently been proposed that an increase in solution conductivity may have the effect of actually promoting a more protective coating on iron in the presence of calcium carbonate film forming precursors (28). Correlation between the electrical impedances and protectiveness of scales and a quantity related to the conductivity of the solution was found. Conductive salts facilitate protective film formation, provided that sufficient temporary hardness exists. This effect is dicussed in more detail under the calcium carbonate film section below.

The other overall effect of dissolved salts, that of decreasing the solubility of dissolved gases, is also illustrated in Figure 7. Since the dissolved oxygen content is the main controlling factor under the conditions, "salting out" of oxygen causes a decrease in corrosion rate. This effect only becomes pronounced at higher salt concentrations and is most likely unimportant in natural fresh waters.

Chloride is the most deleterious individual ionic species normally occurring in natural waters. Much of this appears to be due to the ability of chloride to promote pitting by penetration or local destruction of otherwise protective iron oxide films. It is quite difficult for a uniform, true passive iron oxide film to be formed in the presence of chloride ions. Foley lists five possible specific roles for chloride in iron corrosion (31). It is difficult, however, to quantify the relation of corrosivity to chloride concentration in natural waters. The treshold concentration of chloride, above which pitting of iron is possible, is said to be about 10 ppm (31). The role of sulfate is more nebulous, especially since sulfate does not appear to have the film piercing properties that chloride displays. Larson has done extensive studies of the effect of these salts on corrosion of steel under conditions simulating potable water environments (57, 58, 59, 60). He concludes that the corrosivity of air-saturated domestic waters depends on the following factors (60).

- The proportion of corrosive agents (chloride and sulfate ions) to inhibitive agents (bicarbonate, carbonate, hydroxide, and calcium ions).

- The concentration and degree of effectiveness of the corrosive and inhibitive species.

- The velocity of flow which affects the rates of diffusion of both types of species to the surface.

He also notes that the relative effectiveness of the species involved is not definitive, but may be influenced by one or more of the others. The interdependence of the relevant factors is also emphasized by the observation that "intermediate proportions" of corrosive to inhibitive species, which result in incomplete protection (to uniform corrosion) at a particular solution flow rate, are conducive to pitting and/or tuberculation. Representative results obtained by Larson are shown in Figure 8 (60).

Effect of Dissolved Carbon Dioxide--

The effect of dissolved carbon dioxide depends in large part on solution pH since this determines the relative amounts of "carbonic acid" (hydrated CO_2), bicarbonate, and carbonate present. The carbonic acid form is aggressive towards iron since it can serve as a relatively concentrated reactant for hydrogen evolution at a relatively high pH (23). This effect is probably not very important in aerated natural waters above a pH of about 6. Carbonic acid can also act to dissolve calcium carbonate/hydrated iron oxide films and thus remove protective diffusion barriers.

Bicarbonate is the predominant CO_2 species from about pH 7 to 10. Larson has classified bicarbonate as a mild, but effective inhibitor of steel in aerated natural waters, in the absence of calcium (60). This was a general experimental result but was not explained physically. Recent work by Davies and Burstein in concentrated bicarbonate solutions, borate buffered at pH 8.8, indicates that the anodic dissolution of iron is accelerated by bicarbonate due to formation of the complex $Fe(CO_3)_2^{2-}$ (22). Formation of solid $FeCO_3$ along with $Fe(OH)_2$ is also indicated under some conditions. Pitting is attributed to the heterogeneous nature of the surface reaction products and formation of the complex. This bulk solution is quite different from the bulk bicarbonate content of natural waters, but the results may be relevant to localized corrosion. The environment under a calcium carbonate scale on iron or in a developing pit or tubercule could in some instances have a high effective bicarbonate concentration and aid in initiation or growth of localized corrosion. The effect on uniform corrosion on relatively bare surfaces would still be expected to be minimal. Except as implied by the foregoing, carbonate ions in normal domestic water are expected to be essentially neutral except as they can act beneficially to form $CaCO_3$ films or decrease acidity.

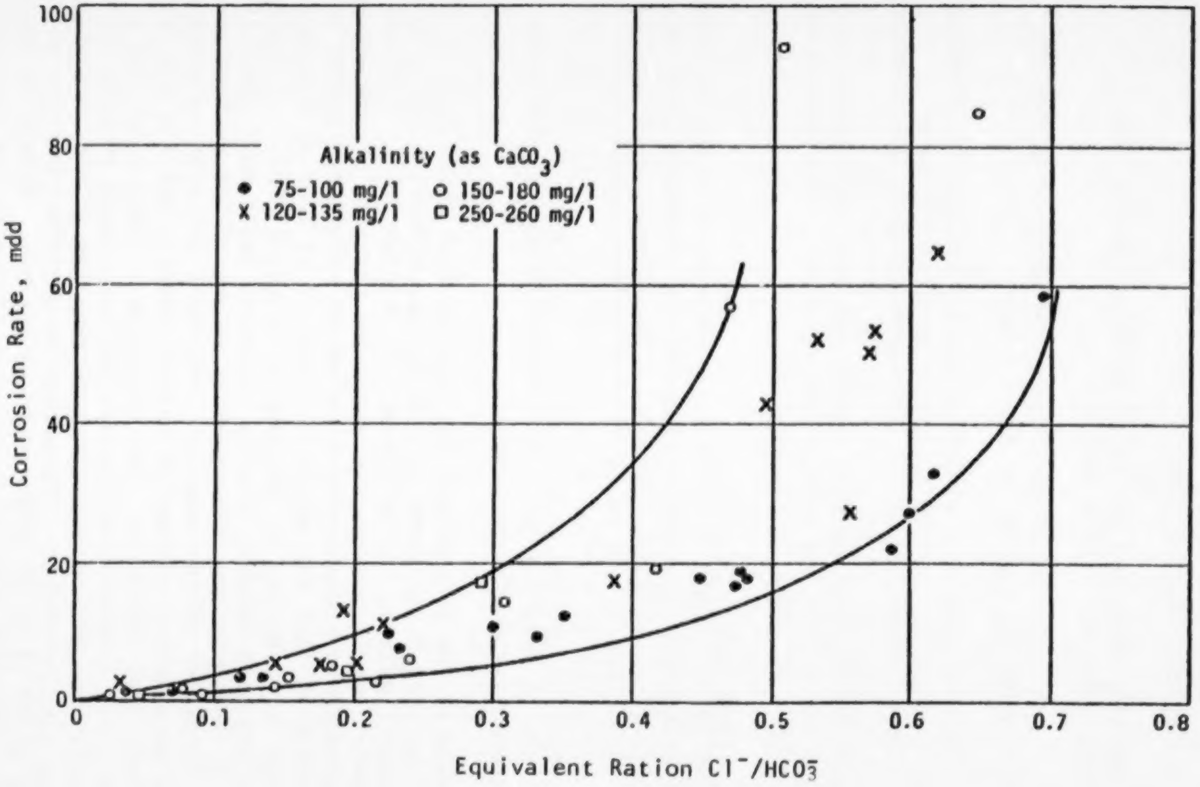


Figure 8. Effect of chloride-bicarbonate salts ratio on corrosion of mild steel (60).

Effect of Calcium--

Much of the protection, both natural and man-made, for iron-based materials in potable water environments is attributed to the formation of a calcium carbonate film or scale on the surface of the material. Presumably, this film provides a diffusion barrier to oxygen, thus further limiting the oxygen reduction rate which is usually rate controlling in natural aerated waters. Various indices have been proposed to approximate the tendency of calcium carbonate to deposit or to dissolve in natural waters, as discussed in Section 2. The actual mechanism of protection, however, is much more complicated than simple deposition of a layer of $CaCO_3$. The saturation indices are often useful as guides, but are too indirect to be applied indiscriminately. Langelier was one of the early proponents of applying a $CaCO_3$ saturation index to corrosion control and described both an index and its correlation with results obtained in New York City pipe corrosion tests (53). He also presented refinements and reviewed early applications (54). The methods do not provide a quantitative measure of the amount or rate of corrosion or $CaCO_3$ deposition. By 1954, Larson noted that water works practice indicated that the saturation index does not necessarily show corrosivity.

Inhibition by calcium carbonate appears to be intimately connected with the corrosion reactions on iron or steel. In a review of treatment methods for desalination product water, Bopp and Reed emphasize that sufficient dissolved oxygen (they quote a minimum of 5 ppm) is needed for the proper formation of protective $CaCO_3$ (+ iron oxide) films (7). Untreated product water will rapidly attack iron and other normal materials of construction of municipal systems. McCauley studied the properties of $CaCO_3$ coatings formed on cast iron under different conditions (67). In general, development of an adherent layer required the initial deposit of dense material well bonded to the metal. Even if this initial layer was very thin, a tenacious coating could be developed. The films formed in static tests produced poorly bonded mixture of calcium, ferrous carbonate and iron oxide in a porous layer of rust. Adherent, durable layers were usually formed under high flow rate conditions on corroded samples. The presence of colloidal $CaCO_3$ was beneficial. These adherent layers developed were largely hydrous ferric oxide (in the form of limonite) with 5 to 40 percent calcite ($CaCO_3$). Siderite ($FeCO_3$) was usually observed close to the metal surface in ridges (67).

Larson reports that calcium, independent of saturation index, is a mild but effective corrosion inhibitor of machined cast iron at least in the presence of sufficient alkalinity (60). The corrosion rate depended on calcium concentration, practically independent of flow velocity from 0.08 to 0.85 fps, pH, minor variations in chloride to alkalinity ratios, and presence or absence of chlorine, chloramine, and silica. It was found that a certain length of time was needed for the effectiveness of calcium to become apparent. The effect was explained on the basis of the corrosion reactions providing an environment at the surface conducive to the formation of $CaCO_3$, even though the bulk water is below saturation with respect to $CaCO_3$.

Stumm measured corrosion rates of cast iron under relatively well characterized conditions (97). Results are shown in Table 6. According to his analysis, neither the $CaCO_3$ saturation equilibrium, nor the relative amount of $CaCO_3$ deposited at the electrode surface are significant parameters of

TABLE 6. CHEMICAL COMPOSITION AND CORROSION CHARACTERISTICS OF WATERS INVESTIGATED (97)

Water Number	Type[a]	Temperature in degree C	pH	Analysis							CaCO$_3$ Deposition, in mg per cm^2		Saturation Index, in pH units	Buffer Caoacity, mg per pH	Corrosion Rate, mg/dm^2 day				
				as mg per L CaCO$_3$					mg per L										
				Ca+2	Mg+2	Alkalinity	Cl$^-$	SO$_4$-2	Si	O	20 Days	50 Days			Ini-tial	5 days	20 days	50 days	100 days
1	Sy	10	7.1	180	0	250	14	20	-	11.0	0.35	0.43	-0.40	1.92	182	37.6	5.2	1.1	-
2	Gr	9.8	7.6	185	69	245	3	20	7	11.0	3.5	3.6	+0.07	0.074	165	45	7.7	2.0	0.5
3	Sy	10	7.1	250	0	250	14	20	-	11.0	0.24	0.31	-0.25	1.92	182	54	10.4	2.3	-
4	Gr	12	7.5	158	37	180	12	-	-	2-4	-	-	-0.20	0.81	106	54	17.6	4.6	-
5	Gr	12	7.4	203	55	228	4	-	-	9	-	0.8	-0.03	1.01	150	57.3	13.0	2.9	-
6	Su	4.7	7.7	124	24	136	2	16	2	11.5	2.6	2.7	-0.40	0.33	80	53	21.8	7.7	1.6
7	Su	6.4	8.0	99	12	103	2	-	2.5	12.2	6.5	9.2	-0.20	0.14	100	59	20.8	6.6	1.8
8	Sy	10	7.0	0	0	250	14	20	-	11.0	0	0	-	2.30	125	67.9	22.2	6.4	-
9	Sy	10	8.2	38	0	83	-	20	-	11	2.4	4.6	-0.40	0.08	111	79.4	38.5	14.2	-
10	Sy	3-5	7.0	40	8	12	-	-	-	12.5	-	-	-2.5	0.11	77	65.0	42.6	22.8	10
11	Sy	10	8.3	20	0	100	14	20	-	11.0	2.5	4.8	-0.50	0.00	83.2	68.9	43.2	21.3	-
12	Sy	10	8.6	38	0	209	-	20	-	11.0	6.1	12.0	+0.30	0.22	156	96	36.7	12	-
13	Su	10	8.4	65	17	47	16	32	-	11	0.03	0.10	-1.6	0.524	105	70.3	48.9	22.9	-
14	Su	10-18	8.5	56	17	47	16	32	-	3-11	2.6	5.3	±0.0	0.045	105	67.1	58.2	25.8	10.4
15[b]	Gr	12	7.1	278	37	285	12	-	-	5-6	-	-	-0.15	2.20	142	105.5	52.4	21.5	-
16	Sy	10	8.0	0	0	250	-	20	-	11	0	0	-	0.28	208	146	63	24.4	-
17	Sy	10	8.1	0	0	180	12	20	-	11	0	0	-	0.17	102	130	71.2	29.2	-

a: Sy = synthetic, Su = surface, Gr = ground water

b: High nitrate and occurrence of iron bacteria corrosion inhibition. He used ground cast iron samples in a number of natural and synthetic waters and exposures over 50 days. The deposition of $CaCO_3$ is primarily controlled by the electrochemical changes at the surface and thus is associated with the corrosion reactions and accompanying pH changes. He also speculates that the buffer capacity of the solution exerts a considerable influence (greater buffer capacity, i.e., alkalinity, being less corrosive) and that the anode/cathode relative area is important and pH dependent. The relative size of the local anode areas supposedly increases with increasing pH. Deposition of $CaCO_3$ is stimulated by elevated pH of local cathode areas but acts to reduce the anode area fraction (97). These considerations make $CaCO_3$ deposition more effective at a pH of about 7 than at higher pH values, and also more effectively applied to well buffered waters.

Patterson contends that effective $CaCO_3$ protection can only be provided when the water contains an alkalinity of at least 50 mg/L (as $CaCO_3$), and an equal amount of calcium (expressed as equivalent $CaCO_3$) (75). Using these minimum values, the pH required to maintain the $CaCO_3$ coating is much higher than the pH calculated using most saturation indices. The $CaCO_3$ layer deposited at a high pH has often been found to be less effective than that formed at moderate pH. Excessively high pH values may promote pitting and tuberculation.

Recent work by Feigenbaum and co-workers stresses the structure of natural calcium/iron scales (27). Fifteen natural scale layers formed in potable water systems carrying waters of various compositions were examined by scanning electron microscopy, x-ray diffraction, and microanalysis. The specimens studied showed a distinct outer zone (adjacent to the scale/water interface) and inner zone (adjacent to the metal/scale interface). The outer zone is relatively compact and consists of contiguous crystals mainly of calcite ($CaCO_3$). The inner zone is considerably more porous and comprised of geatlite [$\alpha FeO(OH)$], siderite ($FeCO_3$), and magnetite (Fe_3O_4) that favor a needle-like and granular porous structure. A steep gradient in Fe and Ca concentrations was found in the bulk scale. Depth of the gradient in the scale varied from scale to scale and appeared to play a role in protectiveness (27). In a later study, these workers proposed a model based on the structure and porosity of the scales they had observed and made AC impedance measurements on scaled specimens to associate with the diffusion resistances used in the model (28). Correlations were developed between the individual impedances of the 15 natural scales and their crystalline phase composition and water composition. A new criterion for the tendency of protective scale deposition was proposed and compared to others. Results of the correlation of scale impedance (spatial compactness) and water quality factors are shown in Table 7. Further comparison of scale resistance with long-term corrosion experience indicated good correlation with the γ value. According to this criterion, provided sufficient temporary hardness exists, the presence of chlorides and sulfates can improve the protective properties of scale (28).

TABLE 7. RESULTS OF CORRELATION ANALYSIS (28)

Number	Combinations	Correlation Coefficient	Standard Deviation
1	$\frac{[Ca^{++}]\,[HCO_3^-]^2}{[CO_2]}$	0.71	52
2	Langelier index	0.34	70
3	$\frac{[Alkalinity]}{[Cl^-] + [SO_4^=]}$	0.49	223
4	$Y = AH + B\,([CL^-] + [SO_4^=])\exp(-1/AH) + C$	0.92	32
	where $A = 3.5 \times 10^{-4}$, $B = 0.34$, $C = 19.0$, and $H = \frac{[Ca^{++}]\,[HCO_3^-]^2}{[CO_2]}$		

Effect of Flow Rate and Temperature--

Examples of the diverse and often opposing effects of solution flow rate on corrosion of iron have been noted in the previous sections of this discussion. The extremes of flow rate can produce serious corrosion: stagnant situations promoting pitting and tuberculation, and very high flow rates causing widespread metal losses due to erosion-corrosion. In the intermediate range, the effect of flow rate on corrosion rate has been modeled (apparently for conditions where velocity dependent $CaCO_3$ deposition or high oxygen passivation do not occur) (66). The equations are based on a double resistance model in which one resistance is significantly time dependent. An adequate representation of new data obtained at 150°F and available literature data was obtained using the semi-empirical correlation and as a function of Re number and a dimensionless diffusion group (66).

The effect of temperature on corrosion of iron in natural water is also highly complex. It has received very little independent study. Temperature changes can affect all of the aqueous equilbria, diffusion rates, deposition rates and electrochemical reaction rates. In relatively simple systems such as when the iron corrosion rate is controlled by diffusion of oxygen through the reaction product film, the rate increases as the increase in oxygen diffusion rate increases with temperature. In this case, the corrosion rate doubles with every 30°C rise in temperature up to about 80°C. Above 80°C, in open systems, the corrosion rate decreases sharply due to the marked decrease in solubility of oxygen with increasing temperature (107).

Effects of Other Species in Solution--

This section gives a brief discussion of the effects of free chlorine, chloramine, nitrate, humic acids, and sulfide on the corrosion of iron in natural waters. Variation of species such as sodium ion, potassium ion, or magnesium ion is not expected to have appreciable effects on corrosion rates.

The effect of free Cl_2 concentration (mg/L) is shown in Figure 9 where they are superimposed on data obtained with no Cl_2 present (60). These results were obtained for mild steel in aerated water of about 120 to 135 mg/L alkalinity, about 30 mg/L NaCl, at pH 7 and 8 and at low flow rates. It can be seen that the corrosion rate is increased in the presence of free chlorine concentrations greater than 0.4 mg/L. As shown, chloramine actually acts as a mild inhibitor at low concentrations. The threshold concentration of free chlorine for accelerated corrosion may be a function of the chloride to alkalinity ratio, but this was not investigated. Chlorine can act as an oxidizing agent which is "stronger" than oxygen in neutral solutions.

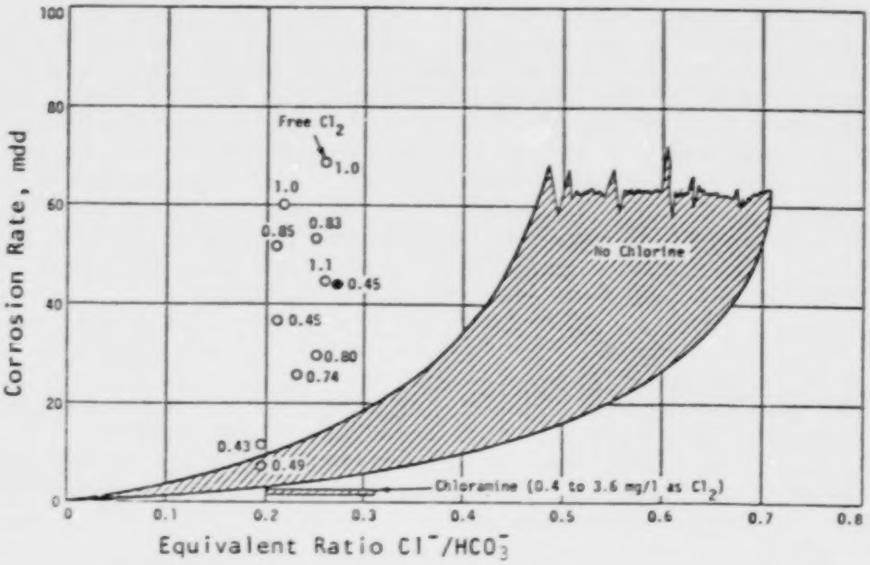


Figure 9. Relative corrosion rates of mild steel at particular chloride-bicarbonate ratios with and without chlorine (60).

Nitrate ion can be reduced on iron and play a role similar to that of oxygen as a "cathodic depolarizer." The thermodynamic driving force is not as high as for oxygen, but there are no solubility limits on nitrate and it can be present under anaerobic conditions. A case has been described in which severe corrosion of a 2.5 mile steel main carrying anaerobic well water was caused primarily by 4-7 ppm (as N) nitrate (12). A detectable decrease in nitrate concentration and corresponding increase in nitrite, ammonia and hydroxyl ion (products of nitrate reduction) and dissolved iron was found as water passed through the main. Increasing the pH from 6.4 to 8.0 completely arrested the corrosion both in the presence and absence of chlorine. Nitrate can under some conditions act as a passivating agent for iron, but this is an undependable type of inhibition.

The effect of humic acids on the corrosion of black steel pipes in natural waters has recently been reported (86). These compounds were found to inhibit corrosion for a range of hardness, flow rate, and chloride values. The authors interpret this as being due to the inhibition by the humic material of the oxidation of the siderite ($FeCO_3$) product layer. They attribute considerable protective properties to siderite layers. It also seems possible that large organic molecules such as these could also act as direct adsorption inhibitors or lead to the formation of reaction product layers whose structure is more protective, regardless of composition.

Hydrogen sulfide or other sulfide species should not be present in any properly maintained water system. In spite of this, cases do arise where water containing sulfides is conveyed to consumers usually from small water suppliers using underground sources (111a). The presence of sulfides is almost always objectionable to the consumer. In addition, sulfide waters can be quite corrosive, attacking iron and steel to form "black water" and also attacking copper, copper alloys, and galvanized piping, even in the absence of oxygen. The mode of attack by sulfide is often complex and its effects may either begin immediately or not be apparent for months only to become suddenly severe. Much of the corrosive action of sulfide may be due to the partial replacement of oxide or hydroxide films on iron or copper by metal sulfide films which either disrupt the normal protective nature of the film or initiate galvanic corrosion. Wells has discussed methods for removal of hydrogen sulfide and sulfides from water in detail (111a).

Comparison of Cast Iron and Mild Steel--

Cast irons are ferrous alloys containing more than 1.7 percent carbon. Gray fracture due to the presence of free graphite is seen in normal slowly-cooled cast form. This graphite causes the brittleness of cast iron and is the important metallurgical difference from mild steel. From a corrosion standpoint, the main differences are:

- a surface skin of iron oxide, silicates, and alumina silicates which is formed on cast iron during production.
- the existence of graphite sites which occur at 0.04 mm intervals on ground cast iron surfaces (57).

- graphitic corrosion of cast iron is possible.

The exterior skin can increase corrosion resistance of cast iron relative to mild steel, but this layer is often partially removed by grinding, especially prior to the application of linings. Grinding exposes the graphite sites, and these can stimulate corrosion relative to steel during initial exposure by galvanic attack. There seems to be little difference between corrosion rates of ground cast iron and steel at long durations. Under some conditions a selective leaching of iron (due to the galvanic cell formed by graphite and iron) can occur ultimately leaving a porous mass consisting of graphite, voids, and rust. This is usually a slow process.

Corrosion of Galvanized Iron

Galvanized (zinc coated) steel is an example of a coating used as a cathodic protection device. The zinc coating is put on the steel not because it is corrosion resistant, but because it is not. The zinc corrodes preferentially and protects the steel, acting as a sacrificial anode. Electrodeposited zinc coatings are more ductile than hot-dipped coatings and usually quite pure. Hot-dipped coatings form a brittle alloy layer of zinc and iron at the coating interface. Corrosion rates of the two coatings are comparable except that hot-dipped coatings, compared to rolled zinc and probably electrodeposited Zn, tend to pit less in hot or cold water. This difference suggests that either specific potentials of the intermetallic compounds favor uniform corrosion, or that the incidental iron content of hot-dipped zinc is beneficial. In this connection, it is reported that Zn alloyed with either 5 or 8 percent Fe pits less than pure Zn in water (107). Zinc used for hot-dip galvanizing may contain 0.01 to 0.1% cadmium and up to 1% lead as impurities (73).

Effect of Water Quality Parameters--

In aqueous environments at room temperature the overall corrosion rate of zinc in short-term tests is lowest within the pH range 7 to 12. In acid or very alkaline environments, major attack is by H_2 evolution. Above about pH 12.5, zinc reacts rapidly to form soluble zincates by the following reaction.

$$Zn + OH^- + H_2O \rightarrow HZnO_2^- + H_2$$

In general, both zinc and cadmium react readily with nonoxidizing acids to release hydrogen and give divalent ions. Cadmium, however, is relatively stable in bases since cadmiate ions, if formed, are much less stable than zincate ions. The effect of pH on corrosion of Cd is shown in Figure 10. In the intermediate pH range of main interest here, the main cathodic reaction in aerated waters is probably reduction of oxygen. The corrosion rate of zinc in distilled water increases with oxygen concentration and with CO_2 from air saturation (105). Nonuniform aeration of the surface can cause differential concentration cells and localized corrosion of zinc. The corrosion rate of zinc increases with temperature as discussed below. In general, corrosion in actual use is greater in soft waters than hard waters (52,108). Chlorine additions, in the amounts normally used for health protection of water supplies, do not increase the corrosion of zinc in water (2).

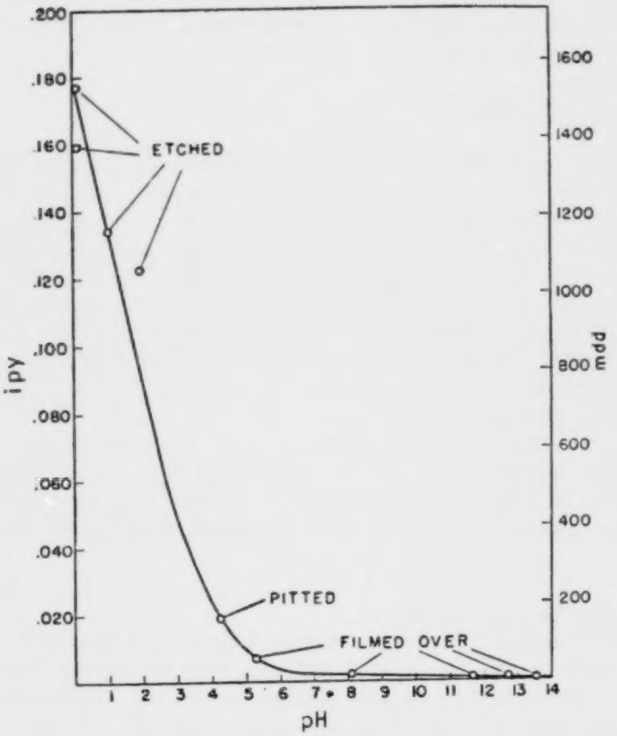


Figure 10. Corrosion of Cadmium vs. pH in continuously flowing, uniformly agitated and aerated solutions of HCl or NaOH (108).

Material: 5 x 10 x 0.63 cm (2 x 4 x 1/4") cast cadmium.

Temperature: 24 ± 0.5°C (74 ± 1°F).

Time: 7 days for pH below 2; 41 days for pH above 2.

Wagner has summarized results from field and laboratory tests on the effect of water quality parameters on corrosion of galvanized steel tubes (109). He shows a definite correlation between corrosion rate and pH, at least for the zinc phase of the coating and with steady flow of water (at 0.5 m/s). These results, shown in Figure 11, indicate that corrosion rate increases rapidly with a decrease in pH in the pH range 7 to 8. This effect is said to exist in spite of other water quality parameters. According to Wagner, there is negligible effect of buffer capacity and saturation index on the corrosion rate of galvanized steel tubes, although the composition of the deposits are altered. Corrosion rate does vary with time, first decreasing as zinc corrosion products grow. Once formed, the coating gives a constant (but pH-dependent) rate as long as the metallic zinc phase is present. Once the Zn/Fe alloy phase is reached, the rate decreases again but reaches another constant value which is also pH dependent. Effects of additives and organic acids are also discussed (109).

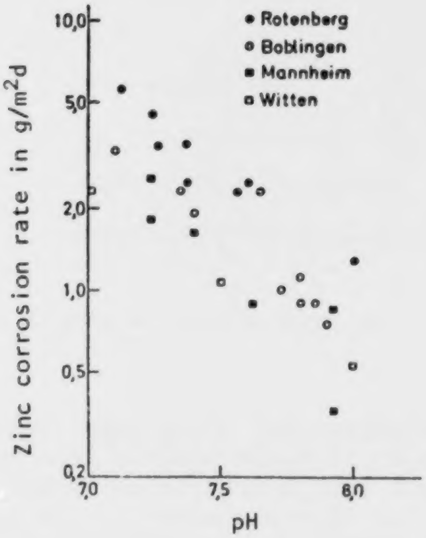


Figure 11. Effect of pH on corrosion on galvanized steel tubes (109).

One of the important environmental factors for galvanized steel or iron is the dissolved copper content of the water. A corrosion study of galvanized steel and galvanized wrought iron pipes in 25 selected domestic waters for two years has been reported (70). Computer correlation of corrosion grades with a large number of factors such as chloride, pH, saturation index, alkalinity, hardness, flow rate, etc. was attempted. The only definite correlation for corrosion of galvanized pipe with water quality was for dissolved copper concentration. Chloride concentration was a possible accelerating factor. In general, the remainder of the results were difficult to interpret. Attack was observed only on the zinc, not iron. There was no evidence that high alkalinity (above 100 ppm) or silica had inhibitory effects. Several case histories illustrating the copper effect are given by Cruse (19). His results, showing the correlation of copper found in corrosion products with maximum pitting rates in potable water, are shown in Figure 12.

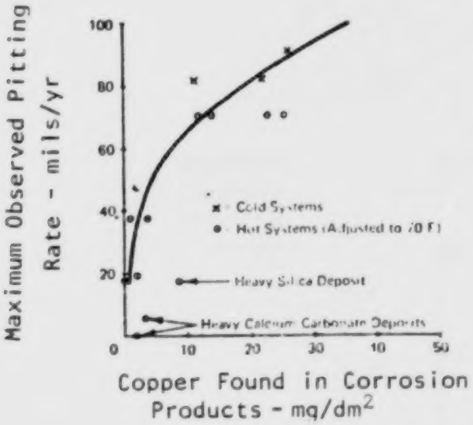


Figure 12. Corrosion of galvanized pipe in potable water systems (19).

Stagnant Conditions--

The increase in concentration zinc, along with cadmium and lead, from hot-galvanized pipes in domestic drinking water systems has recently been discussed (10). Under stagnant conditions, concentrations of 5 to 10 ppm zinc may be obtained after 8 to 40 hour exposure to new galvanized pipes. This behavior is almost independent of water composition. Most of the corrosion products are not dissolved but present as an "oxidic colloid" or finely divided solid. The content of corrosion products in stagnant water could be decreased by treating the water with phosphates or silicates. Their research results indicate stagnation water in new pipes can also contain cadmium and lead products but in rather lower proportion to zinc than their concentration in the galvanizing layer. The authors are apparently referring to tests using piping corresponding to a German standard in which the hot-galvanized coating consists of about 97 percent Zn and 3 percent Fe with maximum limits of 0.8 percent Pb and 0.01 percent Cd.

A field investigation dating from 1973 was also undertaken for new plumbing in a three story building (10). All samples were taken from one tap on the top floor. The water composition is shown in Table 8; initial lead and cadmium contents probably coming from "old pipework." Zinc, cadmium, and lead contents in stagnation waters are shown in Table 9. The scatter in individual measurements is attributed to the corrosion products being mainly present in the form of suspended solids. Taking the initial values of Cd and Pb to be 2 μg/L Cd and 25 μg/L Pb, the concentration increases due to building plumbing and relative amounts shown in Table 10 were obtained. Random samples from the pipe materials in this plumbing system showed a composition of 97 percent Zn, 0.7 percent Pb, and 0.06 percent Cd for the galvanizing layer. This gives ratios of Zn/Cd = 1600 and Zn/Pb = 140 which, according to the authors, indicate some retention of Pb and Cd in the pipe covering layers (10).

TABLE 8. WATER COMPOSITION (10)

Parameter	Content (millimole/L, except as noted)
pH	7.0 - 7.3 pH Units
Alkalinity (to pH 4.3)	3.6 - 4.5
Acidity (to pH 8.2)	0.85 - 1.3
Chloride	1.6 - 2.3
Sulfate	0.93 - 1.33
Nitrate	0.2 - 0.3
Cu^{2+}	< 0.01 mg/L
Cd	1 - 3 μg/L
Pb	20 - 30 μg/L
O_2	3 - 7 mg/L

TABLE 9. ZINC, CADMIUM AND LEAD CONTENTS IN STAGNATION WATER (1-3 DAYS) (10)

TIME OF INVESTIGATION:	1973	1974	1975	1976	1977
Cadmium Contents in μg/L					
Number of Determinations	0	17	9	10	3
Range of Variation	--	2/8	5/10	1/11.6	4.8/10
Mean Values	--	4.6	6.0	5.4	7.6
Lead Contents in μg/L					
Number of Determinations	0	12	9	10	3
Range of Variation	--	20/120	69/90	47/96	25/50
Mean Values	--	56	80	67	39
Zinc Contents, mg/L					
Number of Determinations	12	23	9	10	3
Range of Variation	2.1/9.9	1.9/9.4	5.6/7.1	3.7/6.7	2.1/4.4
Mean Values	6.9	6.7	6.3	5.6	3.5

TABLE 10. CADMIUM AND LEAD CONTENT OF STAGNANT WATER (1-3 DAYS) (10)

Period	Mean Value of Cd (μg/L)	Mean Value of Pb (μg/L)	Zn/Cd (mass	Zn/Pb ratio)
1974	2.6	31	2567	216
1975	4.6	55	1370	115
1976	3.1	45	2100	142

In flowing water the zinc content remained about 8 to 15 ppm for each year from 1973 through 1977, apparently due to extraction from solid zinc compound covering layers. No increase in Pb or Cd (within experimental precision) was noted in flowing water (10).

Comparative tests of galvanized iron in waters having a pH value between 7.5 and 9.5 and containing calcium bicarbonate, but having a very low content of sulphates, chlorides, and nitrates, show that the attack on zinc was soon mediated. But in waters low in calcium bicarbonate or containing appreciable quantities of sulphates, chlorides, or nitrates, zinc suffers pitting attack. Zinc tends to form an insoluble basic zinc carbonate layer on the attacked areas which limits their size. Other findings were that zinc electrochemically protects iron when it is clean, but when coated with a resistant layer of corrosion products the maximum distance at which it still gives protection decreases. Zinc protects the alloy layer of a galvanized coating where it has become laid bare, but the alloy layer will not afford electrochemical protection to bared iron. The calcium carbonate which is deposited on alloy or on iron in the course of electrochemical protection is itself protective, and the ultimate success of the electrochemical protection of any exposed area appears to depend on the building up of the protective effect of this chalk layer at a greater rate than that at which protection is lost by dissolution of zinc from the area adjacent. The thickness of the zinc layer, the calcium bicarbonate content, pH value, and conductivity of the water appeared to be the deciding factors (48).

Hot Water Corrosion--

A number of studies have been performed on the corrosion of zinc in hot water tanks (39, 47). Some of the findings may be summarized as follows:

1. That low alkalinity water containing all or nearly all calcium and magnesium normal carbonates, at a temperature of 150°F, is more corrosive to galvanized metal than water containing no normal carbonates, even though dissolved oxygen is appreciable and some free CO_2 is present.

2. That normal calcium and magnesium carbonates deposit an uneven scale, from 1/32 to 1/16 of an inch in thickness, which is somewhat adherent, whereas the bicarbonates of calcium and magnesium

produce a much thinner scale, probably basic carbonate of zinc, which adheres much better to the metal.

3. That corrosion of zinc depends more upon the alkalinity and pH of the water than upon the dissolved oxygen present.

4. That the attack of normal carbonate water on the galvanized tank, which brings about failure, starts at the pin-holes or the weak spots in the galvanizing. The water soon penetrates through such pin-holes and then attacks the iron. These pits keep spreading and growing deeper until the tank fails.

5. That the products of corrosion fill the pin-holes, thus acting as a protective film.

The effect of temperature on weight losses of zinc was established by using distilled water with aeration and agitation. Weight losses at 150°F were found to be six times greater than at 50°F. This increase in corrosion was found to be caused by a change in the nature of the film from an adherent gelatinous state to a nonadherent granular state. The nonadherent film was found to exist between 131° to 167°F, which is within the range of use in water tanks (39).

In many aerated hot waters, reversal of polarity between Zn and Fe occurs at temperatures of about 60°C (140°F) or above (107). This leads to Zn having the characteristics of a noble coating instead of a sacrificial coating, and hence a galvanized coating under these circumstances induces pitting of the base steel. A 15-year service test on piping carrying Baltimore water at a mean temperature of 46°C (115°F) and maximum of 80°C (176°F) confirmed that pitting of galvanized pipe was 1.2 to 2 times deeper than in black iron pipe (ungalvanized) of the same type, corresponding to shorter life of the galvanized pipe. In cold water, however, pits in galvanized pipe were only 0.4 to 0.7 times as deep as those in black iron pipe, indicating in this case a beneficial effect of galvanizing. It was found that waters high in carbonates and nitrates favor the reversal in polarity, whereas those high in chlorides and sulfates decrease the reversal tendency (107).

The cause of this reversal is apparently related to the formation of porous $Zn(OH)_2$ or basic Zn salts, which are insulators, under those conditions for which Zn is anodic to Fe, but to formation of ZnO, instead, under conditions where the reverse polarity occurs. The latter compound conducts electronically, being a semiconductor. It can therefore perform in aerated waters as an O_2 electrode whose potential, like mill scale on steel, is noble to both Zn and Fe. Accordingly, in deaerated hot or cold waters in which an O_2 electrode does not function because O_2 is absent, Zn is always anodic to Fe, but this is not necessarily true in aerated waters. Apparently, the presence of HCO_3^- and NO_3^- aided by elevated temperature stimulates formation of ZnO, whereas Cl^- and SO_4^{--} favor formation of hydrated reaction products instead.

At room temperature, in water or dilute NaCl, the current output of zinc as anode decreases gradually because of insulating corrosion products which form on its surface. In one series of tests, the current between a couple of Zn and Fe decreased to zero after 60 to 80 days and a slight reversal of polarity was reported. This trend is less pronounced with high purity zinc on which insulating coatings have less tendency to form.

Stainless Steels

According to Reedy, stainless steels used by the water works industry can be divided into the three groups given below (82).

1. Chromium steels (containing 12 percent or more Cr) designated by the American Iron and Steel Institute (AISI) as Type 400 series (best known examples are Types 410 and 430).

2. The 18-8 chromium-nickel stainless steels, designated AISI Type 300 series, of which Types 301, 302, and 304 are frequently used.

3. AISI Type 316 stainless steel with a nominal composition of 18% Cr, 12% Ni, and 2.5% Mo.

Stainless steels are frequently used where protective coatings are not satisfactory or cannot be used such as in corrosive areas of water treatment plants and in components such as pumps, valves, meters, venturis and pressure regulators. Extensive use of stainless steel as a cladding material for uptake and downtake shafts and for control and distribution chambers in a New York City water tunnel has been reported (36). This project will use seven million pounds of stainless steel clad.

The resistance of stainless steels to uniform corrosion is generally good, but overall corrosion stability depends on maintenance of a passive state. Passivity in the sense used here is described below. Maintenance of the corrosion resistant state depends on both the particular type of stainless steel employed and on the environmental conditions.

Passivity--

The corrosion resistance of stainless steels depends primarily on the ability of the material to achieve and maintain a passive state in an aggressive environment. The ability to achieve a passive state determines the reduction in uniform corrosion rate from that of an active metal. The ability to maintain the integrity of the passive state determines the resistance of the material to local attack caused by the chemical environment, eroding particles, or stress. This passive state is characterized by a certain electrode potential or limited potential range over which the dissolution rate changes from a relatively high to a relatively low value. The electrode potentials associated with the onset of passivity and the maximum current density needed to reach the passive state from the active state are a function of the metal composition, chemical composition of the environment, and temperature.

The detailed mechanism of formation and exact nature of the passive surface components have been a subject of controversy for many years. It is probable that primary protection is offered by a very thin (on the order of 10 to 100 angstrom, amorphous, pore free metal oxide film. The film should be an electronic conductor. Thicker, more porous crystalline layers formed on top of the thin passive layer may offer substantial barriers for chemical or mechanical attack on the basic film. However, the primary corrosion resistance is dependent on the initial establishment of the passive layer and its continued stability. The type of passivity defined here should be distinguished from that attributed only to the formation of sparingly soluble reaction products on a metal surface. The latter process, which can be predicted from Pourbaix diagrams, does not necessarily imply an established passive state and the absence of corrosion. It is essential that the reaction products be formed directly on the metal surface and as a direct consequence of the anodic reation; complex processes such as chemisorption may also be intimately involved.

Localized attack occurs when momentary passive film breakdown, in the presence of chloride, exposes a small part of the metal surface which is surrounded by a large film-covered cathodic area. The cathodic area can drive anodic metal dissolution at the bare spot at a high rate (high current density). Once started, hydrolysis of metal ions from the anodic reaction causes the pH in the incipient pit or crevice to decrease which in turn discourages film repair and augments attack. Growth involves migration of chloride into the area which can also augment corrosion. Much of the greater resistance of the more resistant materials is probably due to their greater rate of film repair so that pit initiation is much less likely.

Type of Corrosion and Effect of Alloy Composition--

Passivity in relatively mild environments is obtained by alloying iron with at least 12 percent chromium. The stainless steels formed with more than 12 percent Cr as the only major added component, typified by the Type 400 materials, generally show relatively low uniform corrosion rates in typical potable waters. They are highly susceptible, however, to severe localized corrosion (pitting, crevice, and weld related attack) in waters containing chloride and oxygen (37, 82, 96). Additional alloying is needed to obtain resistance to localized corrosion, but even the more resistant alloys are occasionally susceptible to local breakdown of passivity. Type 400 materials are not recommended for submerged service in potable water systems (82). The stainless steel most favorably used for such service is probably Type 304, which with 18 percent Cr and 8 percent Ni, has much better localized corrosion resistance. Addition of about 2 percent molybdenum (and more nickel) to Type 316 generally gives higher resistance to chloride induced pitting and crevice corrosion than Type 304. While uniform corrosion rates are low for Type 300 materials in potable water environments (36, 37, 96), their application must be well understood to avoid localized attack. Good welding procedures and design to eliminate crevices are particularly important. More resistant types than Type 316 are known, but they are mainly used in extremely corrosive process industries.

Environmental Effects on Corrosion of Stainless Steels--

The two most important chemical factors in potable water systems are chloride and oxygen. Oxygen plays a conflicting role in the corrosion of stainless steels. Oxygen is necessary for the maintenance of the passive state for many stainless steels, but it also provides the driving force for local disruption of the passive film in the presence of chloride to give localized corrosion. The susceptibility of a given material to localized attack increases with chloride concentration. Sulfate and perhaps bicarbonate appear to act as pitting inhibitors and their concentration relative to chloride is a relevant factor (61). The solution pH in the neutral region has relatively little effect on pitting of 300 series stainless steels (M. J. Johnson in Reference 3).

Temperature can have a major effect on the localized corrosion of stainless steels. Susceptibility to pitting increases with increasing temperature for both Types 304 and 316 and the change is fairly marked for moderate (15-30°C) temperature increases above 25°C. Scale and other deposits decrease the corrosion resistance of stainless steels since they provide an opportunity for establishment of differential aeration cells and for crevice corrosion. Stagnant areas can be deleterious for similar reasons. High flow rates can usually be tolerated, in the absence of eroding debris or entrained solids, in the liquid phase. Careful design is needed to ensure satisfactory performance of these materials.

Results in Potable Water--

While stainless steels have been tested under a variety of conditions in the chemical process industry and laboratory, relatively few direct tests in potable water systems have been reported. Results have been reported for Type 410 and Type 316 in Southern California waters including treated Colorado River water (96). Type 410 was stable in four aqueduct and well waters, but was very severely corroded by pitting in both treated and untreated Colorado River water. Since pH and dissolved O_2 were nearly the same in most cases, the reason for increased corrosivity of the Colorado River water may have been its high chloride content (85 ppm) relative to the other waters (16-28 ppm). Type 316 was completely undamaged in any of the waters (96).

Extensive tests of a variety of stainless steels in New York City Reservoir water have been reported (36,37). A typical average analysis of this water is shown in Table 11. Results obtained during exposure in a semi-stagnant area in a shaft 14 feet above the main flow are shown in Table 12. Type 416 was not submerged. The pitting rates for the 300 series materials and 17-4 PH (a cast stainless steel) are all quite small. Weight loss corrosion rates did not exceed 0.01 mpy (36). Similar results were later reported at longer exposures (up to 15 years) for samples submerged in jars containing periodically renewed samples of the same water (37). A submerged Type 416 sample suffered severe crevice corrosion in these tests. Other results were essentially the same; no attack was noted on 300 series or 17-4 PH materials.

CORROSION OF COPPER IN POTABLE WATER SYSTEMS

Copper is a highly regarded material for use in potable water service lines. It is flexible, easy to join and install, has a low resistance to flow, and is considered to be fairly resistant to the corrosive action of most waters. Corrosion can occur under certain conditions, however, causing a number of water quality problems. Most of these problems have been

TABLE 11. TYPICAL AVERAGE ANALYSIS OF NEW YORK CITY RESERVOIR WATER (Catskill-Delaware System--1969) (37)

Component	Concentration (mg/L) (except as noted)
Alkalinity (as $CaCO_3$)	5 - 14
Calcium	3 - 6.3
CO_2	1.8 - 4.0
Chloride	4.0 - 7.0
Copper	0.01 - 0.10
O_2	13.7 - 14.3
Hardness (as $CaCO_3$)	19 - 23
Sulfate	6.0 - 14.0
Silica (as SiO_2)	0.5 - 2.5
Total Solids	40 - 54
pH	6.5 - 7.5
Specific Conductivity (μmho)	60 - 73

TABLE 12. STAINLESS STEELS--PITTING IN RESERVOIR WATER (36)

Alloy	Test Duration (years)	Maximum Pit Depth (mpy)
304	2	0.25
304L	9	0.23
316	9	0.11
316L	9	0.11
317	9	0.34
17-4 PH	2	0.05
416[1]	4	7.20

[1] Exposure at 100 percent humidity and 23°C.

NOTE: Each item represents average of 3 or more specimens.

delineated by an AWWA task group report and are summarized as follows (16). Small concentrations of copper cause the formation of blue or blue-green stains on procelain fixtures. Concentrations greater than 1.0 ppm react with soap to produce insoluble green "curds." A bitter, unpalatable taste results from copper when it is present in concentrations greater than 1.0-1.5 ppm. Traces of copper can accelerate the corrosion of galvanized hot-water tanks and cause pitting of aluminum pots and pans. Traces of copper are objectionable in many industries, i.e., in those involved in the canning of foods and in those using metallic-plating baths. Small amounts of copper in irrigation water are toxic to sugar beets and barley grown in nutrient solution. A concentration of 2 ppm or more is believed to be toxic to tomatoes. Copper is toxic to fish in concentrations of 0.25-1.0 ppm. Pitting corrosion may lead to the failure of copper pipe as a result of pin-hole leaks.

Corrosion of copper in potable waters has been the subject of numerous studies and papers. There are many factors which influence the corrosion process. The interdependence and frequent lack of independent control over these factors has led to a rather chaotic literature. However, favorable conditions for the corrosion stability of copper must predominate in most cases of potable water use based on its overall record. From World War II to 1972 over 6 million miles of copper plumbing tube was put into service (15). Relatively few cases of actual failure have occurred.

General Considerations

Although many modes of corrosion of copper have been distinguished, this discussion will classify the types of corrosion of interest here into only two types: general or uniform corrosion and localized corrosion. Velocity-related corrosion will be discussed under localized corrosion. These modes encompass the most prevalent ones from a water quality standpoint. Their basis is interrelated to a certain degree. It often appears that conditions which suppress uniform corrosion can give way to localized corrosion.

In the total absence of oxygen, copper is thermodynamically incapable of corrosion in potable water environemnts. The usual presence of at least some oxygen is the driving force for corrosion of copper in these environments, but it is not usually the determining factor. It is doubtful that total exclusion or removal of oxygen from potable water systems is desirable or economically feasible. Such efforts could in fact be deleterious due to the formation of sulfide, ammonia, or related compounds by bacterial action which could be harmful to copper or other materials, especially if they are eventually exposed to waters containing oxygen or other oxidants.

Given the presence of oxygen and possibility of corrosion, the actual occurrence of copper corrosion is governed by the presence and stability of inorganic compound films on copper. Probably the most noteworthy of these from a corrosion standpoint is cuprous oxide (Cu_2O) formed by initial corrosion of copper. As will be noted, the mode of formation is very important. Films of cuprous oxide formed by annealing or other manufacturing steps may be detrimental to the stability of the basic metal.

The protective, metal-solution-grown layer of cuprous oxide may be very thin and subject to further attack by solution species and physical erosion. The cuprous oxide layer is often formed slowly and is tenuous in comparison to the type of passive films which offer much of the corrosion protection to metals such as iron, nickel, cobalt, and chromium. As such, it is fortunate that other, thicker, films of insoluble copper compounds are often formed over the primary film and can offer mechanical protection from erosion and an additional barrier to diffusion by aggressive chemical species. Films formed by deposition of calcium carbonate and similar compounds can offer similar, but still somewhat unnatural, forms of protection. But the most basic protection is offered by the delicate, and often slowly grown, thin layers of cuprous oxide. For this reason, conditions occurring during the initial service exposure of copper are very important. Moderate flow rate and chemically mild environments favor formation of small grained, compact and protective layers of Cu_2O. Rapid deposition of disordered Cu_2O under harsher environments may be deleterious since the first layer is not very protective. At high flow rates in aggressive environments, growth may be delayed or very slow. Growth of localized layers of materials such as copper sulfides may be very harmful due to their galvanic influence on adjacent areas of metal.

The dynamic nature of these processes must also be kept in mind. Materials in service are often subjected to stresses which demand more or less continuous maintenance of a protection mechanism.

Uniform Corrosion of Copper--

From experience, the uniform corrosion rate of copper is usually quite low in potable water systems. This observation is based on the long life of the majority of tubing in service. From a health standpoint, however, low corrosion rates over a large uniform surface area can add a significant amount of impurity to a relatively small volume of water. Therefore, although low uniform corrosion rates may be acceptable based on corrosion lifetimes, they may be significant from a water quality viewpoint.

Selected literature results on uniform corrosion of copper in potable waters are given below. Emphasis is placed on references which are illustrative of the literature as a whole. It is noteworthy that the maximum reported copper concentration in standing water of reasonable pH is about 5 ppm and that this value is reported quite often. This could indicate that copper concentration is ultimately limited by solubility of a reaction product.

Effect of O_2

The simplest overall electrochemical uniform corrosion mechanism for copper, requiring simultaneous oxidation and reduction at the material/solution interface, can be represented by the parallel reactions Eqs. 5 and 6.

$$Cu \rightarrow Cu^{2+} + 2e^- \qquad (5)$$

$$1/2O_2 + 2e^- + 2H^+ \rightarrow H_2O \qquad (6)$$

There is evidence that, at least in acidic solution, O_2 is also involved in reaction with intermediate Cu^+ as in the following more elementary steps including the "chemical" step (Eq. 8).

$$Cu \rightarrow Cu^+ + e^- \qquad (7)$$

$$Cu^+ + O_2 + 2H^+ \rightarrow Cu^{2+} + H_2O_2 \qquad (8)$$

As previously mentioned, in the total absence of oxygen copper is thermodynamically incapable of corrosion in potable water environments. This was substantiated by Schafer's study of corrosion of copper pipes in potable water service in New Zealand (89) where a negligible amount of corrosion was reported in the absence of oxygen. However, the amount of oxygen needed for corrosion to occur may be small. Tronstad and Veimo (105, 106) determined that varying the oxygen content of the tap water between 2.7 ppm and 25 ppm had a relatively small effect on the final dissolved copper concentration. With 100 ppm added $NaHCO_3$ (pH 7.0) the copper cencentration increased about 50% for the 10-fold oxygen increases, while with 500 ppm $NaHCO_2$ (pH 7.2) the copper content increased by about a factor of 3 over the same oxygen range. The authors attributed this to oxidation of dissolved cuprous compounds.

Effects of pH

The effects of pH on copper corrosion have been studied in direct and indirect tests. In their work with water standing in copper tubes, Tronstad and Veimo (105, 106) measured the copper concentrations in water after 24 hour exposure of tubing to tap water alone, and with various additions of oxygen, carbon dioxide, sodium bicarbonate, sodium hydroxide, and calcium oxide. The tap water composition and pertinent experimental details are given in Table 13. All experiments were done at 18°C in the closed tubes.

This tap water can be classified as soft, having a fairly low pH, moderate amount of aggressive CO_2, low alkalinity, and moderately high oxygen content. In the tap water alone, the copper concentration reached a maximum of 0.6 ppm after about 15 hours and then slowly declined. Addition of sodium bicarbonate raised the pH but also consistently raised the amount of copper dissolved over a 24-hour period. For example, addition of 0.4 g/ℓ $NaHCO_3$ produced a pH of 7.2 and dissolved copper of 1.9 ppm. Addition of calcium bicarbonate had a similar effect. Addition of carbon dioxide lowered the pH and increased both the copper content and rate at which a maximum was reached. For example, 9 ppm CO_2 gave a pH of 5.65 and copper content of 3.9 ppm after 24 hours; with 45 ppm CO_2, a copper content of 4 ppm was reached after only 2 hours.

Addition of sodium hydroxide or lime to the tap water caused a decrease in the copper concentration observed after 24 hours until a pH between 8 and 9 was reached. Above a pH of about 10, the copper concentration increased once again. The lime additions resulted in somewhat lower copper concentrations, at the same pH, than sodium hydroxide additions.

TABLE 13. CONDITIONS OF COPPER DISSOLUTION EXPERIMENTS OF TRONSTAD & VEIMO (105)

Tap water composition:

Total solids	47.5 ppm
Ash	28.5 ppm
Chlorides as $C\ell^-$	9.5 ppm
Iron	0.07 ppm
Combined CO_2	8.0 ppm
Free (aggressive) CO_2	4.0 ppm
pH	6.3
$KMnO_4$ consumed	65 $m\ell/\ell$ of 0.01 N $KMnO_4$
NH_3, NO_x, phosphates	Not detected

Properties of copper tubing:

Purity: 99.8 to 99.9%

Treatment: annealed, bent into loops, descaled in 2 N NH_4OH, washed with distilled water

Specimen Size:

Volume: 99 cm^3

Internal surface area: 785 cm^2

Internal diameter: 0.5 cm

Length: 500 cm

Experimental studies under simulated domestic use conditions were done to determine the effect of pH on copper corrosion and were reported by an AWWA Task Group (16). The water composition was not specified, but apparently it was aerated and contained CO_2. In the first set of experiments, water at an adjusted pH value was allowed to flow through 60 feet of new 0.75 inch copper tubing at a rate of 0.067 gpm (0.05 fps). Samples were collected at the end of 1 hour and again after 1.25 hours, the copper concentration determined, and the two values averaged. The observed copper concentrations as a function of pH are shown in Figure 13.

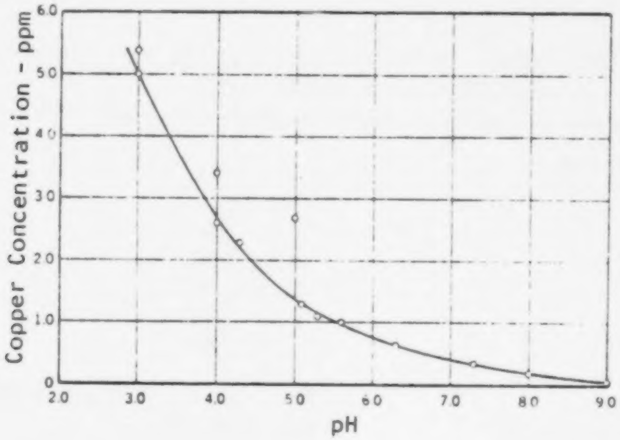


Figure 13. Effect of pH on corrosion of copper (16).

In the second type of experiment, water at the desired pH was passed through new copper tubing of the same dimensions at a flow rate of 0.5 gpm (0.37 fps) for 1 hour. The flow was stopped and the water allowed to stand in the tubing for 16 hours (to simulate overnight conditions). The flow was then started again with water at the initial pH and rate. Water samples were collected immediately and at various time intervals and analyzed for copper. Results as a function of time and pH are shown in Figure 14. The exponential decay suggests a simple rinsing effect of the dissolved copper solution formed during the stand.

The Task Group concluded from these two sets of tests and others that the carbon dioxide content of a water (indirectly measured by its pH) has a very significant effect on the corrosion solubility of copper (16). In addition, raising the pH to a value above 7.0 "greatly minimizes" this action.

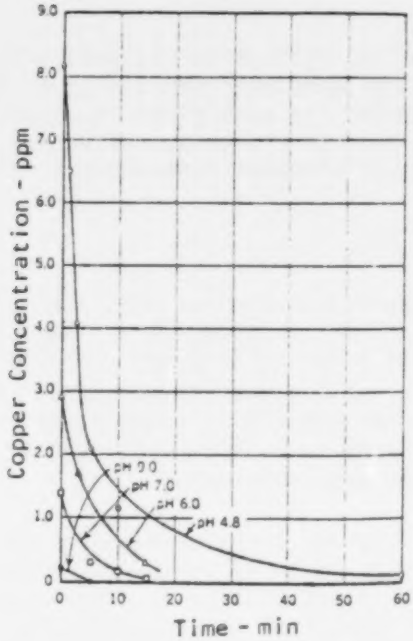


Figure 14. Effect of time and pH on corrosion of copper (16).

Effect of Free CO_2--

The free CO_2 or carbonic acid content of natural waters has often been reported to play a significant role in the uniform corrosion of copper. This could be due to its acting as a source of hydrogen ions at the surface since the free CO_2 concentration can be many times the bulk hydrogen ion concentration. Free carbon dioxide may also act to dissolve or thin the protective films on copper, thus enabling higher corrosion rates. Both mechanisms could occur in practical systems. The amount of CO_2 necessary to cause increased corrosion in potable waters probably depends on many factors. A concentration of 10 ppm is often quoted as a rule-of-thumb "threshold" concentration for anticipating or diagnosing CO_2 corrosion problems.

A review of early results on corrosion of copper and brass pipe and the relations to health is given by Hale (40). His general conclusions are that:

- Soft waters containing very little free carbonic acid will show little corrosion of copper or brass pipe.
- Soft waters containing considerable free carbonic acid (10 ppm and up) may corrode copper and dezincify yellow pipes.

Several examples were given for soft, high CO_2 waters in which standing copper concentrations of 5 ppm were obtained and up to 3.9 ppm with water running continuously. Examples are also given in which treatment to remove the CO_2 by pH adjustment and/or aeration were effective in controlling the corrosion of copper. Aeration of water containing little natural oxygen is, of course, discouraged.

Effects of Temperature

In their previously mentioned studies (105, 106) Tronstad and Veimo also investigated the effect of elevated temperature. Copper concentration measurements were made at different times at 46°C and 70°C and the data were corrected for the change in solubility of CO_2 with temperature. Although the initial rate of copper dissolution increased with temperature, the maximum concentration in solution did not change much, apparently due to solubility limitations and consumption of the available oxygen.

Schafer (89) obtained copper corrosion data by sectioning and measuring pipes that had been in service up to 30 years. He found that corrosion in hot or previously heated water was usually less than in the same water before heating, presumably due to removal of dissolved CO_2 and O_2 at elevated temperatures. Most corrosion appeared to occur in the first few years after installation.

Effects of Miscellaneous Parameters

Low concentrations of iron (0.05 to 0.5 ppm Fe^{2+}) have been found to inhibit the corrosion of copper in service such as seawater desalination. This concentration of iron could be dependent on the previous contact of water with steel or cast iron pipe. The effect should be considered when evaluating or designing tests of copper corrosion rates. It also raises the possibility that much copper pipe is "protected" by upstream iron pipe.

The distinction between surface and artesian waters may also be of interest in connection with reports of a natural inhibitor of localized corrosion of copper. This unidentified, probably organic inhibitor, is said to occur in most surface waters but not in underground waters (13). However, the distinction between surface and artesian waters noted by Schafer with regard to copper corrosion rates in cold (normally 10-20°C) potable waters was that:

- Surface waters usually showed a corrosion rate below 0.5 mpy (to a first approximation) irrespective of pH, hardness, chloride, and other water properties.

- In low pH, high carbon dioxide artesian waters containing moderate amounts of oxygen, corrosion was more rapid than in surface water and rates up to 15 mpy were observed.

A report of high concentrations of copper from 12-14 month old copper service lines in one district in England has been given (8). The chemical composition of the initial potable water was not reported. Initial morning water samples from houses in towns 12 miles apart both showed maximum copper concentrations of 5.5 ppm. These were serviced by 65 foot lengths of 0.5 inch copper tube. Four consecutive-day samples from one of these houses had copper concentrations within the narrow range of 4.8 to 5.5 ppm. Other results given in the paper do not indicate any correlation of copper concentration with length of service pipe. Based on the limited data given, the copper concentration does appear to vary inversely with pipe diameter, which could be due to the change in surface to volume ratio. Results are shown in Table 14.

TABLE 14. COPPER IN INITIAL MORNING SAMPLE OF WATER FROM COPPER PIPES (8)

Sample	Type of Pipe	Diameter (inch)	Length (feet)	Copper Concentration (ppm)
A	copper tube, welded joints	1.25	6000	0.75
B	soft copper tube, mechanical joints	0.50	65	5.5
C	copper tube, mechanical joints	1.00	1740	1.2
D	hard (straight) copper tube	0.50	15	3.2
E	soft (underground) copper tube	0.50	60	4.8 - 5.5

NOTES:

1. Samples A, B, C - all from same main
2. Samples D, E - from 2 houses in a town 12 miles away
3. All pipe said to be to British Standard Specifications, in service for 12 - 14 months.

The same report states that copper content at any house during normal day-time use did not exceed 0.5 ppm (8). Equipment was installed at one house to dispense a "slowly soluble" hexametaphosphate to the water. This caused the copper content of initial morning water samples to drop from a consistent average 5 ppm to an average of 2 ±0.2 ppm (samples from 8 different days). This relieved complaints of "blue water" and morning vomiting.

Fluoride in the concentrations added to many domestic water supplies (up to 1 ppm) has no effect on the amount and rate of corrosion in copper distribution systems (62, 63). Sulfide is discussed in the section on iron.

Localized Corrosion of Copper--

In this report, localized corrosion of copper will include pitting, impingement, and under-deposit forms of attack. Pitting is probably the most common of these and will be discussed at some length, followed by a shorter discussion of impingement. Under-deposit attack, a form of crevice corrosion, has been observed for copper, but its occurrence should be relatively rare for copper in potable water systems. However, when it does occur in hot water systems, attack can be rapid (89).

The pitting of copper is a complex phenomenon which probably has several different causes and a number of different contributing factors. The problem is apparently not widespread, but it has recieved considerable attention since failure of practically new pipe or tubing can occur in a short time. Even in a given water distribution system, the failures often occur at random locations.

The effects of copper pitting on potable water quality are difficult to assess. The actual area of material that is affected is usually small and the pits themselves are often capped with corrosion product which prevents significant loss of soluble copper to solution. On the other hand, while active pitting is occurring, the rate of attack per unit surface area is much higher than the usual rate of uniform corrosion. Also, pits may rupture unpredictably from time to time, releasing small amounts of concentrated copper ion solutions. Copper in solution can promote the corrosion of other metals, as discussed elsewhere in this report.

Causes of Pitting--

Much of the difficulty in characterizing copper pitting is in distinguishing between factors which initiate pitting and those which are necessary to sustain it. Possible synergism between these factors also complicates matters.

There are several elaborate theories on the growth and structure of corrosion pits on copper (17, 26, 64, 80). These models do not appear to be particularly helpful in determining either the probability of pit initiation or the tendency of a given water to support pitting.

Campbell has distinguished between two forms of copper pitting (13). The first form, called "soft-water pitting," occurs only in certain soft waters containing manganese. It usually is restricted to the hottest parts of hot water systems and is associated with formation of a scale of manganese oxides which forms an unfavorable galvanic couple with any exposed copper surface. The second type, hard-water pitting, occurs in hard or moderately hard waters and is nearly always restricted to cold water pipes. Campbell states that this type of pitting is usually associated with the presence of either a carbon film or a "glassy" copper oxide scale formed when certain abnormal conditions prevail during the annealing process. These films are cathodic to the copper surface and either one can provide a galvanic driving force which induces pitting.

The second form of pitting is prevalent in England and has promoted considerable study (17, 81). Its occurrence is apparently prevented by a naturally occurring organic inhibitor which is present in many surface waters, but not in well waters. The inhibitor has not been isolated, but it is removed by activated charcoal and has been further characterized (13).

The presence of carbon films on copper pipes manufactured in the United States is said to be rare (43, 111). At least one possible case of pitting due to a carbon film has been reported (111). Evidence has been presented for pitting due to a "glassy" copper oxide scale in U.S. Service lines by Cruse and Pomeroy (20). These authors examined over 65 pipe specimens. Although carbon films were present, the correlation with tendency to pit was less for carbon content than for the presence of glassy cuprite scales. They conclude that well water containing dissolved oxygen, relatively high mineralization, and a pH below 7.5 is conducive to the rapid pitting of copper, but that such pitting occurs only where the copper surface is sensitized by relatively heavy glassy cuprite scales, carbon residues, or perhaps other deposits or scratches.

From a survey conducted in the United States, pitting of copper tubing has almost invariably been associated with cold, hard well waters, according to Coher and Lynam of the Copper Development Association (15). They state that a typical aggressive well water contains greater than 5 ppm dissolved CO_2, dissolved oxygen up to 10 to 12 ppm (which may come from storage and handling of the well water), and chlorides and sulfates. Their statistical survey also shows that pitting failures are almost evenly distributed between soft or annealed temper and hard drawn tube. They state that this refutes hypotheses based on pitting due to surface conditions of the tube. They also state that pitting can be prevented by treatment of the water to neutralize the dissolved carbon dioxide. A case history discussing the effects of O_2 and CO_2 is presented in Section 6.

Impingement Attack and Flow Rate Effects--

Copper is more susceptible than most engineering metals to a flow-velocity dependent type of corrosion generally termed impingement attack (42). This is usually a localized attack caused by excessive liquid flow velocities and aggravated by the presence of entrained solids or gas bubbles. The resulting metal pits are undercut on the downstream ends and are frequently horseshoe shaped.

The rate of attack depends to some extent on water composition. The rate increases with increasing oxygen content and chloride content. Impingement attack rate increases with decreasing pH. Prevention can be obtained by limiting flow velocity to 5 feet per second for most municipal waters and to considerably lower values if entrained solids or air bubbles are present (43).

Copper Alloys--

A wide range of copper alloys are used in potable water systems, particularly as valve parts or other components where their mechanical properties are desirable. These alloys are divided here into the general classes of brasses, bronzes, and copper-nickel alloys and each is discussed below. The discussion of copper corrosion can be used as a basis for the behavior of the alloys, but their corrosion resistance also depends on alloy composition. One major difference compared to pure copper is that selective leaching is a predominant mode of corrosion for some common copper alloys. This is a corrosion process whereby one consituent of an alloy is removed from the metal, leaving an altered residual structure. A common form of selective leaching is dezincification of brasses. The fundamental mechanisms of selective leaching are a subject of disagreement (44). One view is that the entire alloy dissolves and then one of its components is replated from solution. Another group contends that one component is selectively dissolved from the alloy leaving the porous residue of the more noble species. Others believe that both modes of corrosion occur.

Corrosion of Brasses--

The common brasses are alloys of copper with 10 to 50 percent zinc. A number of other elements may be added either singly or in combination. These elements are listed in Table 15, but not all of these are commonly added to commercial Cu-Zn alloys (108). Hundreds of modifications of the brasses are known. Zinc dissolves in copper up to 39 percent to give a single phase alloy, α brass. Another single phase alloy, β brass, is formed with 47-50 percent zinc. At intermediate zinc levels, the alloy contains both phases, α and β brass (11).

TABLE 15. RANGES OF COMPOSITION OF Cu-Zn ALLOYS (108)

	Percentage
Lead	0.1 to 12
Aluminum	0.1 to 3.0
Tin	0.5 to 6.0
Nickel	0.5 to 10 (sometimes up to 30)
Iron	0.1 to 2.0
Silicon	0.1 to 2.0
Manganese	0.05 to 5 (sometimes up to 25)
Phosphorus	0.01 to 0.10
Arsenic	0.01 to 1.0
Antimony	0.01 to 0.1
Gold	0.5 to 1.0
Bismuth	0.1 to 3.0
Vanadium	0.1 to 0.5
Tungsten	0.1 to 2
Chromium	0.05 to 0.5

Many brasses corrode in major part by dezincification. Two general types of dezincification are recognized, the layer type and plug type. Layer type attack occurs fairly uniformly along the surface while plug type attack is localized and penetration occurs perpendicularly into the metal. Brasses generally resist impingement attack better than pure copper (107). They are susceptible to stress corrosion cracking under certain conditions but this is not discussed here. Pitting can occur under some conditions but this is generally similar to copper and less important than dezincification. Generally, the brasses show very good resistance to most types of unpolluted waters, with corrosion rates averaging 0.1 to 1 mpy, in the absence of dezincification (108). Soft waters containing high CO_2 can cause higher rates, often accompanied by dezincification.

Dezincification is also generally favored by the following conditions (62, 79, 107):

- elevated temperatures,
- stagnant solutions, especially if acid,
- porous inorganic scale formation and crevices,

- residual stresses and local deformation, and
- chlorides and copper ion buildup.

The composition of the alloy is also important. Brasses containing 85 percent copper or more (red brasses) are generally resistant to dezincification. Additions of iron or manganese to brass tend to accelerate dezincification while additions of low concentrations of arsenic, antimony, phosphorus, bismuth, and tin have been used to reduce the rate of dezincification (62). Thus, for example, Muntz metal, common yellow brass, and noninhibited aluminum brass are considerably less resistant than arsenical Admiralty brass and arsenical aluminum brass (108). Layer-type dezincification tends to occur more frequently for high zinc brasses and acidic environments. Plug type attack seems to occur more often for low zinc brasses and neutral, alkaline, or slightly acidic conditions (32). Many exceptions to these general statements can occur, however.

The influence of dezincification on water quality was demonstrated by extensive early work of Clark (14). Unfortunately, the pipe material was only designated as "brass"; it was probably yellow brass (67-33 Cu-Zn) or similar high zinc alloy. Water from several northeastern water supplies was allowed to stand in, or was passed through lengths of new pipe. In general, about the same amount of copper was dissolved from either pure copper or brass pipe. Brass pipes, however, yield much more dissolved zinc than copper (14).

Detailed observations of the corrosion of yellow brass and Muntz metal pipes in domestic hot water systems using several municipal water supplies (78). After 20 to 25 years service, the rate of uniform corrosion was low, but most samples exhibited local corrosion. Corrosion proceeded in two distinct phases, dezincification and then final corrosion of the copper formed. The lag between the two phases varied considerably. In α/β brass pipes the β phase was always attacked first. Initiation of the localized corrosion was often associated with signs of residual stresses. Evidence was found that the copper deposits were residual rather than formed by the redeposition mechanism (78).

A recent study of valve stem brass corrosion in hot and cold potable water at eleven cities in the United States has been reported (18). Commonly used silicon red brasses (Cu-Zn-Si two phase alloys) were tested for one year, primarily in cities where corrosion had been noted. Dezincification of the uninhibited materials was severe and widespread. Addition of 0.03 to 0.06 percent arsenic prevented dezincification in both hot and cold water while similar phosphorous levels were effective only in cold water. No correlation could be found between water composition and dezincification for the cities studied. Temperature was a most important external variable, greatest attack occurring in hot water services (18).

Corrosion of Bronzes--

Originally, the term bronze was used for alloys of tin in copper (here called tin bronzes), but it is now generally applied to casting alloys based on copper whether or not tin is present. The tin bronzes are essentially solid solutions of tin in copper. The most common wrought forms contain 1-10 percent tin. Alloys with more than 8-10 percent tin are usually used in the cast form. There are a number of modifications of Cu-Sn alloys, most of which deal with variations in the concentrations of tin, zinc, lead, and phosphorous. About twelve other elements have been added singly or in combination, although seldom more than four are added at one time. A summary of compositions is given in Table 16 (108). Additions of iron, antimony and bismuth are said to be dangerous and are tolerated only up to 0.2 to 0.5 percent (11). Aluminum bronzes generally contain up to 9-10 percent aluminum as the important minor constituents in copper and sometimes small additions of manganese and copper. Silicon bronzes contain up to 4.5 percent silicon and minor additions of manganese, zinc, iron, or tin (62).

TABLE 16. RANGES OF VARIOUS COMPOSITIONS OF Cu-Sn ALLOYS (108)

	Percentage	
Copper	60.0 - 99.5	
Tin	0.5 - 35.0	
Zinc	0.5 - 15.0	(sometimes up to 30)
Lead	0.5 - 15.0	
Phosphorus	0.01 - 3.0	
Cadmium	0.5 - 1.0	
Nickel	0.10 - 15.0	
Iron	0.05 - 4.0	
Silicon	0.05 - 2.0	
Aluminum	0.5 - 2.5	
Arsenic	0.5 - 2.0	
Antimony	0.1 - 8.5	
Cobalt	5.0	not common
Platinum	10.0	
Tungsten	10.0	
Manganese	3.0	
Bismuth	0.5	

There is relatively little information on the corrosion behavior of the bronzes in domestic fresh waters. Corrosion considerations for the tin bronzes are generally similar to those for copper. The attack by water depends on oxygen, carbon dioxide, and dissolved salt content and the formation of protective layers. Selective leaching of tin (destannification) has been noted, but apparently occurs only under relatively extreme conditions such as in superheated steam or for pump impellers handling hot feed water (11). Alloys containing more than 5 percent tin are especially resistant to corrosion by impingement (107).

Aluminum bronzes are said to show generally superior corrosion resistance to other common copper alloys in sea water service (11). However, selective leaching of aluminum can occur under ill-defined conditions. These alloys are normally more resistant than copper and most brasses to erosion corrosion or impingement attack. Several aluminum bronze samples exposed for 12 years to stagnant New York City Reservoir water showed rather extensive pitting with some cracking (37). Several tin bronzes exposed under the same conditions showed essentially no pitting and average corrosion rates less than 0.02 mpy. Extensive attack was noted for K manganese "bronze" (65% Cu 22% Zn 2% Fe 6% Al 4% Mn). Additional results for a number of copper alloys are given in References 36 and 37.

Silicon bronzes are used where high strength is required along with corrosion resistance comparable to copper. In many environments the corrosion rates are about the same as pure copper (62). The silicon bronzes are more resistant to acid attack and corrosion resistance increases with silicon content.

Other Copper Alloys--

Alloys based on copper and containing 5 to 40 percent nickel have generally excellent corrosion resistance in sea water, brackish water, and fresh water. These copper-nickel alloys are often used in heat exchangers for sea water or for other brackish water applications where ordinary copper alloys do not perform well. The 70/30 Cu/Ni and 90/10 Cu/Ni alloys are most often found, with small additions of iron and manganese to improve corrosion resistance under flow conditions (11, 62). Limited reference has been found to the use of these materials in domestic potable water systems. Extended testing of 90/10 and 70/30 cupronickels with 1 percent iron in New York City Reservoir water showed superior resistance to pitting corrosion. Weight loss general corrosion rates were reported 0.2 to 0.4 mpy (36) and 0.01 mpy (37). Several nickel-copper alloy (Monels) specimens showed significant pitting under the same conditions. Selective leading of nickel (denickelification) form copper-nickel alloys can occur under special circumstances, but it is relatively rare (11).

CORROSION OF LEAD IN THE WATER WORKS INDUSTRY

Because of its favorable structural characteristics, lead has been used for transporting and distributing potable waters in the U.S. since the nineteenth century. From an engineering standpoint, lead is highly resistant to corrosion and attack by natural waters. It is also, however, an active accumulative toxicant, and the distribution of corrosive water through lead pipe can constitute a serious health hazard to the consumer. The current standard for lead, as established by the EPA, is 0.05 mg/ℓ in drinking water. There are indications, however, that this standard may not provide a sufficient margin of safety for the fetus and children under three years old. The National Academy of Sciences has concluded that a lead standard greater than 0.025 mg/ℓ cannot assure a no-observed-adverse-health-effect status (50). Lead corrosion and high lead levels in potable waters have been identified in several municipalities throughout the nation from systematic surveys and sampling procedures. However, because of the expense and difficulty in implementing a comprehensive sampling program, possible lead contamination in many other communities has yet to be identified.

The most common use of lead in the water works industry is for lead service and residential pipes and for lead-based solders. Lead is also widely used as a pipe lining for zinc galvanized iron pipe to enhance durability and extend the useful life of the pipe. Lead is used for "goosenecks" in smaller piping systems to prevent undue stress on water mains, but some utilities have discontinued this use in favor of less potentially harmful materials.

Lead and lead-lined galvanized pipe have a useful life expentancy of 35 to 50 years and longer. Consequently, many of the lead service lines installed are still in operation. Many of the older municipalities in the nation have a large number of lead service lines ranging in length from 30 to 100 feet, which connects the street main to the household plumbing.

The most commonly used lead-based solders are composed of 50 percent tin and 50 percent lead or 60 percent tin and 40 percent lead. During installation, this solder may flow inside the pipes at the joint, thereby providing a lead-based surface area exposed to potentially corrosive water.

A secondary use of lead in the water works industry is for lead gaskets used as flanges for joining large valves and pipes in water treatment plants and on water mains. However, exposed lead surface areas are relatively small and water contact time is usually short minimizing the potential for additional lead contamination.

Lead is also used for the production of brass and bronze. Brass is a copper-zinc alloy which contains up to 12 percent lead, and bronze is a copper-tin alloy which contains up to 15 percent lead. These materials are corrosion resistant and are not suspected of contributing significantly to lead contamination of potable waters. However, test results indicate some dezincification in some brass, and it is reasonable to conclude that lead may also be leached into the water system.

Little information has been compiled which identifies or qualifies the extent to which lead is used in the water works industry throughout the U.S. The most comprehensive survey was completed by Donaldson and the results were published in 1924 (24). His study included a survey of more than 500 water distribution systems in 41 states and concluded that approximately 48 percent contained lead lines. In the Boston metropolitan area, Worth estimated that approximately 60 percent of the residences were serviced with lead pipes (114). In a report published by EPA, it is estimated that approximately 1300 of 3300 service lines in Bennington, Vermont consist of lead (83). Bennington, Vermont is considered a typical New England community. Patterson is currently conducting a survey of the quality of potable water at 1000 consumer's taps across the nation, and because the lead content of tap water is usually proportional to the amount of lead in the plumbing system, this study may indicate the extent of lead use in potable waters (76, 92). Specific areas within a given city may contain greater percentages of lead service lines, and these areas may be identified by a historical review of plumbing codes and pipe sales correlated to the time of development of the area.

In some municipalities where lead corrosion and potable water contamination have been documented, such as in Boston, Massachusetts, local or state plumbing codes restrict the use of lead for soldering only. However, several widely adopted codes, including the Uniform Plumbing Code and the Building Officials Conference of America (BOCA) Code, currently allow the use of lead pipe for transporting and distributing potable waters. Additionally, some municipalities assume responsibility only for water mains and reserve the selection and installation of water service lines to the home owners or builders. Consequently, lead service lines are still being installed and lead solders are widely used.

The primary water quality parameters related to lead corrosion and corrosion rates are hardness, alkalinity, pH, total dissolved solids, dissolved oxygen, and carbon dioxide. At least one investigator also attempted to identify the effects of chlorine content on the corrosive nature of potable waters. Although much research has been presented relating these parameters to lead corrosion, other investigators maintain that the actual contributing factors are not "hardness" but hardness in association with the corresponding anionic component; not alkalinity but the "inorganic carbonate concentration"; and not TDS but possibly specific components or the effect of the ionic strength of the water (34). Much of the literature reported here is written in terms of the traditional parameters (hardness, alkalinity, TDS), however, the factors noted above should be kept in mind when reviewing the corrosion literature. Nevertheless, research should continue to determine the specific mechanisms that contribute to the reported correlations and contradictions. Physical characteristics of the water system such as water velocity also influence lead corrosion. The length of time the lead pipe or material has been in service will also affect the corrosion rate. New lead pipe or materials are more susceptible to corrosion than older or used materials.

The occurrence of lead corrosion in potable water supplies is most prevalent among utilities which distribute corrosive or "aggressive" waters through lead pipes. In general, soft waters containing dissolved oxygen, carbon dioxide, and organic acids are corrosive to lead. However, many investigations completed to date have addressed the corrosive effects of a combination of parameters rather than a single parameter because of the interactive effects. Thus, in reviewing the literature, the reader should reflect on (1) how the parameter being correlated to corrosion reflects the actual corrosive mechanism, and (2) whether this mechanism, as reflected by the parameter, stands alone or is influenced by other factors inherent in the investigation.

Effect of Flow Rate and Volume of Water Flushed--

Because corrosion is a rate process, lead concentrations in water exposed to lead surfaces will generally reach higher levels in standing water than in running water and, consequently, a range of concentrations can be expected from a given sampling point. In a survey of homes in Worcester, Massachusetts completed in 1975 by O'Brien, nine pairs of water samples were collected to compare lead concentration in standing water and running water (74). The results of that survey are provided in Table 17 and show that lead concentrations up to 1.90 mg/ℓ were observed in standing water while no lead concentrations were observed in running samples.

TABLE 17. RESULTS OF WORCESTER LEAD SAMPLING ANALYSIS PROGRAM
(Lead Concentration, mg/ℓ) (74)

LOCATION	STANDING	RUNNING
A	0.05	0.00
B	0.08	0.00
C	0.10	0.00
D	0.06	0.00
E	0.04	0.00
F	0.00	0.00
G	0.06	0.00
H	0.17	0.00
I	1.90	0.00

Wong and Berrang investigated potential sources of lead contamination from water supply facilities using lead service pipes and lead-based soldering to join copper pipes (113). In their investigation, they developed correlations between volume of water flushed through the sytem and observed lead concentrations for water supply facilities which were used only on occasion. The results of their study are shown in Tables 18 and 19. This study showed a decrease in lead concentration with increasing volume of water flushed. It is important to note that very high lead concentrations were observed from the facilities which were not used for an extended period of time.

TABLE 18. LEAD IN WATER TAKEN FROM AN OCCASIONALLY USED TAP 24 HOURS AFTER LAST FLUSHING (113)

Volume of Water Flushed Through Tap (ℓ)	Lead Concentration (ppb)
0.005	130
0.020	130
0.060	240
0.125	410
0.310	330
0.615	60
1.220	16
2.425	17
300.000	7

TABLE 19. LEAD IN WATER TAKEN FROM A TAP NOT USED FOR ABOUT SIX MONTHS (113)

Volume of Water Flushed Through Tap (ℓ)	Lead Concentration (ppb)
0.005	300
0.025	3,000
0.055	2,300
0.105	2,100
0.210	2,500
0.415	490
0.920	190
1.920	64
6.920	15
200.000	12

Effects of Dissolved Oxygen

Slunder and Boyd (95) discuss results reported by other investigators concerning the influence of dissolved oxygen on lead corrosion. They indicate that while some authors maintain that lead is insoluble in air-free pure water, others claim that lead is noticeably soluble in pure water free from gases. Despite these discrepancies, there is general agreement that dissolved oxygen increases the corrosion of lead. Slunder and Boyd present the results of Burns' work (Figure 15) showing that lead corrosion in distilled water is directly proportional to the partial pressure of the oxygen in the atmosphere above the water. An oxygen-nitrogen mixture was used, the test waters were saturated with the mixture, and an adequate pressure was maintained over the water surface during the test.

Slunder and Boyd, also stated that lead in a carbon dioxide-free water is strongly corroded because a protective film cannot form on the lead surface. In the reported experiment, the lead surface became coated with small crystals of lead oxide and hydroxide, the water became turbid, and lead concentrations rose to as much as 100 mg/ℓ. Specifics of this investigation were not presented.

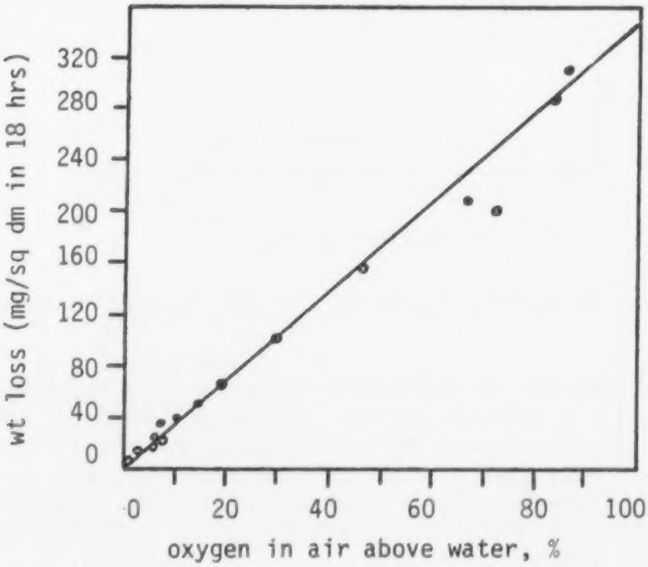


Figure 15. Effect of Oxygen on Corrosion of Lead Submerged in Distilled Water at 75°F (95).

Effect of Hardness--

M. R. Moore of the University of Glasgow attempted to develop a relationship between the rate of lead corrosion and water hardness (68). In his investigation, he synthesized hard water by the addition of calcium chloride to distilled water and measured the rate of dissolution. The results of this study are shown in Figure 16. As is shown, he determined that the dissolution rate decreased exponentially with hardness. However, the specifics of this evaluation were not presented, and it has been suggested that the increased Ca^{2+} and Cl^- contents might have altered the CO_2 absorption tendency, the pH, and hence the lead solvency (34).

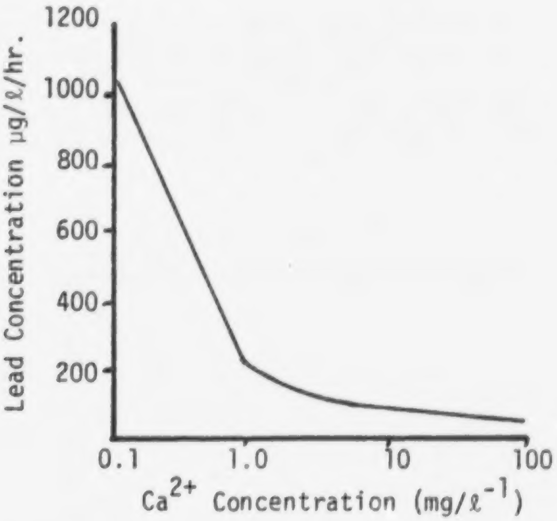


Figure 16. Effects of synthetically hard water on lead corrosion (68).

Others imply that the anions associated with the hardness component are the important factor. In a summary report, Slunder and Boyd explain that most natural waters contain some hardness components which will react with lead to form adherent films, such as calcium carbonate, on lead surfaces which will be protective and prevent further corrosion (95.) According to Slunder and Boyd, a water hardness of 125 ppm as $CaCO_3$ is sufficient to form the protective film and prevent corrosion.

To minimize possible anionic interferences, Naylor and Dague (71) used calcium nitrate and magnesium chloride to produce desired hardness levels. They determined that, in general, variations in the amount of hardness cations had only small effects on lead solubility at the experimentally maintained pH of 10.5.

In soft, aerated waters, corrosion and corrosion rates are dependent on water softness and dissolved oxygen. In general, the softer the water and the higher the dissolved oxygen concentration the greater the corrosion. Additionally, the presence of organic acids whose lead salts are soluble promotes corrosion. Water containing carbonic acids that dissolve calcium deposits will encourage corrosion by forming soluble calcium bicarbonate according to the reaction (95).

$$CaCO_3 + H_2CO_3 \rightleftarrows Ca(HCO_3)_2$$

Effects of pH--

In another experiment, Moore investigated the effects of pH on lead dissolution from a lead pipe (68). In this experiment, water was allowed to stand in a lead pipe section for one hour with pH, adjusted by HCl or NaOH addition, being measured both before and after this time period.

The results of this study are shown in Figure 17 and indicate that the rate of dissolution in distilled water increases considerably on both sides of the pH range from six to eight with a minimum of approximately 1000 µg Pb/liter/hour near pH 6.5.

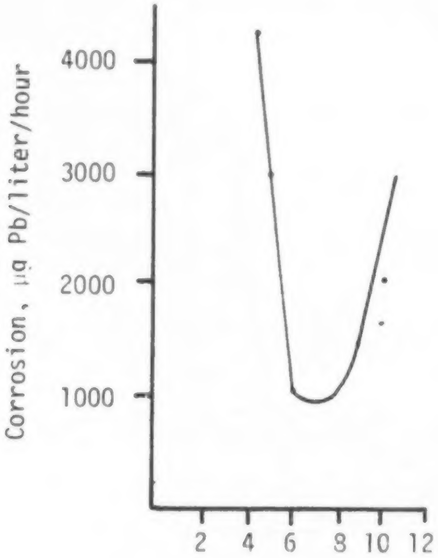


Figure 17. pH effects on lead corrosion (68).

Naylor and Dague (71) indicate that in a solution of pH 8 or less, lead ions will predominate. In the pH range of 8-11, lead precipitates as the lead oxide:

$$Pb^{2+} + 2OH^{-} = PbO \downarrow + H_2O$$

However at a pH > 11, this oxide will dissolve according to:

$$PbO + 2H_2O = Pb(OH)_3^{-} + H^{+}$$

Their experiments on lead control by conventional lime and lime-soda ash water treatment methods produced the lead solubility curve presented in Figure 18. Between pH 9.2 and 10.4, the lead levels were generally < 0.05 mg/ℓ although lead had been added at a rate of 2 mg/ℓ prior to pH control.

When reporting on the occurrence of lead in river systems, Hem and Durum (45) produced soluble lead-pH diagrams with respect to several concentrations of total dissolved carbon dioxide species. Their data indicated that the solubility of lead should be lower than 10 ug/ℓ above pH 8.0, regardless of the alkalinity of the water. However, at a pH near 6.5, and in water with low alkalinity (less than 30 mg/ℓ as HCO_3^-) the soluble lead concentration could range from 40 ug/ℓ up to several hundred micrograms per liter.

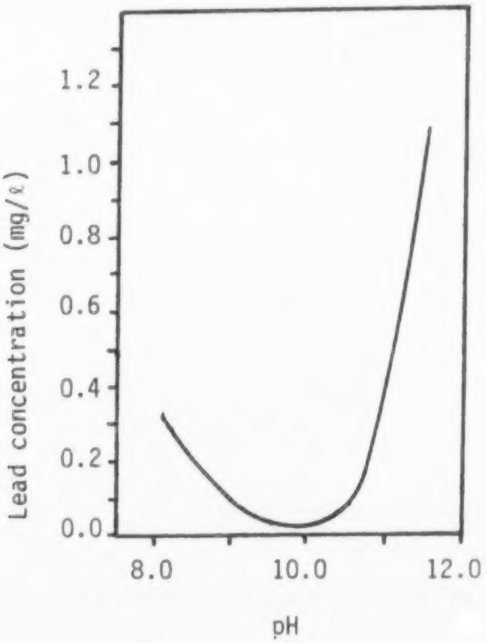


Figure 18. Effect of pH on Lead Solubility (71)

Effects of pH and Hardness--

Several studies have been completed which correlate lead corrosion with soft acidic waters. Karalekas et al monitored lead concentrations in delivered potable waters at five municipalities and correlated the results with raw and finished water quality (50). Table 20 is a summary of the results of their study. Lead concentrations were monitored for water standing in the interior household plumbing overnight, for water standing in the service line, and for water from the main. These samples are identified in Table 20 as Samples 1, 2, and 3, respectively. Lead concentrations in finished water were below the detectable limit of 0.005 mg/ℓ for all municipalities surveyed.

As can be observed, the water systems at Bridgeport, Connecticut and Providence, Rhode Island which have higher pH values and hardness concentrations experienced the least corrosion. Although the water supply at New Bedford, Maine has a pH comparable to Bridgeport, the hardness concentration is lower and the average lead concentrations are considerably higher. In the case at Providence, Rhode Island, indications of lead corrosion are nearly eliminated by maintaining a pH of 10.1 and a hardness concentration of 40 mg/ℓ. In this study, no differentiation was made between particulate lead (detached from the pipe or an un-adhering fresh precipitate) and lead truly in solution (34).

In another study by Karalekas et al, the effects of water quality, primarily hardness, on lead corrosion were investigated for the cities of Boston, Cambridge, and Somerville, Massachusetts (49). These cities were selected for the investigation because many of the homes in these three cities are known to have lead or lead-lined water service pipes. Boston and Somerville obtain water from the same source. In this investigation, both running and standing water samples were collected. Characteristics of the finished water supplied are shown in Table 21.

TABLE 21. CHARACTERISTICS OF FINISHED WATER SUPPLIED TO CAMBRIDGE, BOSTON, AND SOMERVILLE (49)

Parameter	Cambridge	Boston & Somerville
pH	6.9-8.0	6.0-7.0
Total Dissolved Solids (mg/ℓ)	170	30
Chloride (mg/ℓ)	50	7
Hardness	56	14

Water supplied to residences in Cambridge is higher in pH and hardness concentrations than water supplied to Boston and Somerville. As expected, the percentage of samples exceeding the lead standard of 0.05 mg/ℓ was higher in Boston and Somerville than in Cambridge as shown in Figure 19. Additionally, the percentage of households having detectable levels of lead was higher in Boston and Somerville than in Cambridge as shown in Figure 20.

TABLE 20. RESULTS OF INVESTIGATION OF WATER QUALITY ON LEAD CORROSION (50)

	Finished Water Quality			Average Lead Concentration Observed*			
Municipality	pH	Hardness (mg/ℓ)	Alkalinity (mg/ℓ)	mg/ℓ	mg/ℓ	mg/ℓ	Highest Lead Concentration Observed mg/ℓ
Bridgeport, CT	7.1	48	18	0.010	0.011	<0.005	0.04
Marlborough, MA	6.5	14	6	0.014	0.037	0.010	0.250
Chatham, MA	6.3	20	3	0.017	0.018	0.015	0.098
New Bedford, MA	7.3	12	24	0.076	0.090	0.013	0.260
Providence, RI	10.1	40	20	<0.005	0.006	<0.005	0.050

*SAMPLING INSTRUCTIONS PROVIDED:

After 11:00 p.m., do not use the kitchen cold water faucet until collecting the water samples the next morning. Using the following directions, in the morning, collect the water samples at that faucet before using any faucet or flushing any toilets in the house. Fill the provided containers to one inch below the top and put the caps on tightly.

SAMPLE 1. Open the cold water faucet and immediately fill bottle #1 and turn off the water, recap this bottle.

SAMPLE 2. Turn the faucet on and place your hand under the running water, and immediately upon noticing that the water turns colder, fill bottle #2. Cap bottle #2.

SAMPLE 3. Allow the water to run for three additional minutes and then fill bottle #3. Cap bottle #3.

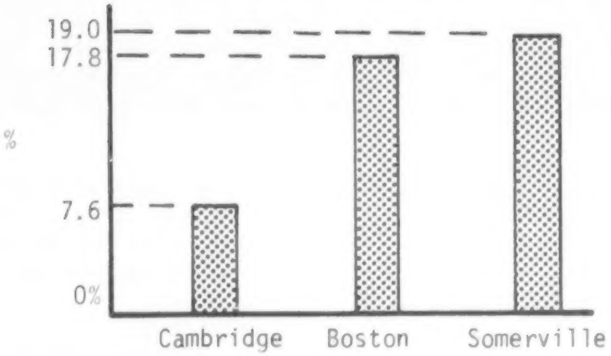


Figure 19. Percentage of samples exceeding lead standard (49).

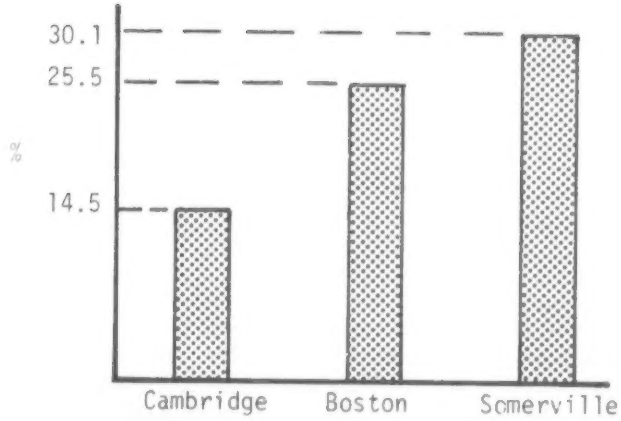


Figure 20. Percentage of households exceeding lead standard in one or more samples (49).

Effects of Alkalinity--

Moderate carbonate alkalinity concentrations have been found to be beneficial in controlling lead corrosion. The presence of this alkalinity will encourage the formation of a very insoluble lead carbonate salt film on the corroding lead surface. This film will adhere to the lead surface and form a protection from the corrosive environment as well as limit lead solubility (77).

In a sampling program to determine the extent of lead in potable water in Boston, O'Brien found that approximately 29.6 percent of the samples analyzed had lead concentrations in excess of 0.05 mg/ℓ (74). O'Brien concludes that the naturally low alkalinity of approximately 4.0 mg/ℓ as $CaCO_3$ is responsible for this high lead concentration occurrence. He also points out that the alkalinity is further depressed by an additional 2.6 mg/ℓ with the addition of hydrofluorosilicic acid to provide 1.0 mg/ℓ of fluoride ion. However, a review of the analysis of water resource characteristics for this study indicate that the water is very soft with a calcium and magnesium concentration of only 2.8 and 1.0 mg/ℓ, respectively. Additionally, the water is slightly acidic with a pH of approximately 6.3. Therefore, this source of water is highly corrosive and it is difficult to specifically identify low alkalinity as the primary cause of high lead levels in Boston's potable water.

The chemical constituency of the protective film is a function of the dissolved species, including hydroxyl, concentrations. Computer generated Eh-pH diagrams presented by Schock indicate that a lead-hydroxy-carbonate, $Pb(OH)_2(CO_3)_2$, may be the predominant solid (91). The tendency to form this hydroxyl-carbonate decreases as the dissolved Pb(II) species concentrations decrease from $10^{-6.0}$M to $10^{-6.62}$M or as the total carbonate concentration increases from $C_T = 10^{-3.7}$M to $10^{-2.7}$M. Solid $PbCO_3$ is reported to form only under low pH, high $[Pb^{++}]$ concentrations.

In a recent investigation, Thibeau et al, used Raman and infrared spectroscopy to analyze the surface film composition of potentiostatically oxidized lead samples in 0.1 M sulfate solutions (100). The results of these analyses were then compared with the composition predicted by the calculated Eh-pH diagram. Only partial agreement existed between the actual observations and the predictions based on thermodynamic equilibria. The major discrepancies were that PbO, although not predicted by the diagram, was found in neutral and basic solutions, and $PbO-PbSO_4$, the compound predicted to be stable under such conditions, was not. Thus, while Eh-pH diagrams may be an aid in interpreting free energy data, their application to the real world problem of corrosion is limited by (1) their assumption of equilibrium conditions, and (2) their disregard for the effects of other species present. For instance, the presence of ions that form soluble lead salts, such as nitrates, will interfere with the formation of protective films and result in increased corrosion (95), and the influence of sulfates or chlorides should be further investigated, especially in regard to corrosive ground waters used in areas with lead service lines, such as in the Dakotas.

While moderate levels of carbonate alkalinity have been shown to help control lead corrosion, excessive concentrations may, in fact, enhance corrosion. Schaut attempted to duplicate actual distribution conditions and study the corrosive action of various water quality parameters on lead pipe. In one test, he exposed new lead pipe to waters with various alkalinity concentrations over various contact periods. Results of this test indicated that for short contact periods, i,e., less than three hours, alkalinity concentrations have little or no effect on lead corrosion. However, for contact periods of 24 to 48 hours using cool water ranging from 35 to 40°F, he determined that lead concentrations in the water were almost doubled as alkalinity concentrations were doubled. Using water at a higher temperature, the effects of increased alkalinity concentrations were not as pronounced. Tests on old lead pipes, which were approximately 35 years old, gave slightly different results and the effects of increased alkalinity were not as obvious. However, increased corrosion rates were observed with increased alkalinity concentrations. Schaut explains that this difference is due to the formation of a basic lead carbonate which is relatively passive to the range of alkalinity used or observed in drinking water. Schaut did not report the values of alkalinity concentrations which he used (90).

In the investigations of lead removal by conventional water treatment methods Naylor and Dague (71) maintained a 200 mg/ℓ alkalinity (as $CaCO_3$) and varied the pH of their water. As expected, lead concentrations of < 0.1 mg/ℓ were found up to a pH of 8.6 in solutions initially prepared with 2 mg/ℓ lead. At higher pH, and contrary to expectations resulting from their previous work on pH effects (see Figure 18), the lead levels rose to 0.9-1.1 mg/ℓ. Because their investigations included various water treatment unit operations, Naylor and Dague felt that physical, rather than chemical, parameters were responsible for this increase in lead solubility.

Current research at the EPA, Municipal Environmental Research Laboratoreis (MERL) in Cincinnati shows similar results with respect to alkalinity concentrations (35). Studies are being conducted to evaluate the effects several water quality parameters have on lead corrosion. Dr. Marvin Gardels is currently examining changes in alkalinity and changes in pH for water treatment to minimize corrosion. Results to date indicate that corrosion may be enhanced with increasing alkalinity by carbonate addition above approximately 40 to 50 mg/ℓ as $CaCO_3$. Gardels has found that increased pH with a depressed carbonate concentration produces the least aggressive waters. From his research, it appears that an optimum combination of pH and carbonate concentration probably exists for maximum protection against corrosion. Initial results indicate, however, that the optimum pH values may be slightly above 9.0.

On the other hand, Schock presented computer generated activity ratio diagrams (constant Eh) for the total lead (II) soluble species in relation to pH, and dissolved lead (II) versus total carbonate concentrations for several pH values. The results from his studies are shown in Figures 21 and 22. He substantiated the activity ratio diagrams with laboratory data and concluded that the possibility of lead control by alkalinity-pH adjustment was not as great as previously believed, and that in the pH range of 8-9.5, there is little advantage to increasing the carbonate level above 30-40 mg/ℓ as $CaCO_3$ (91).

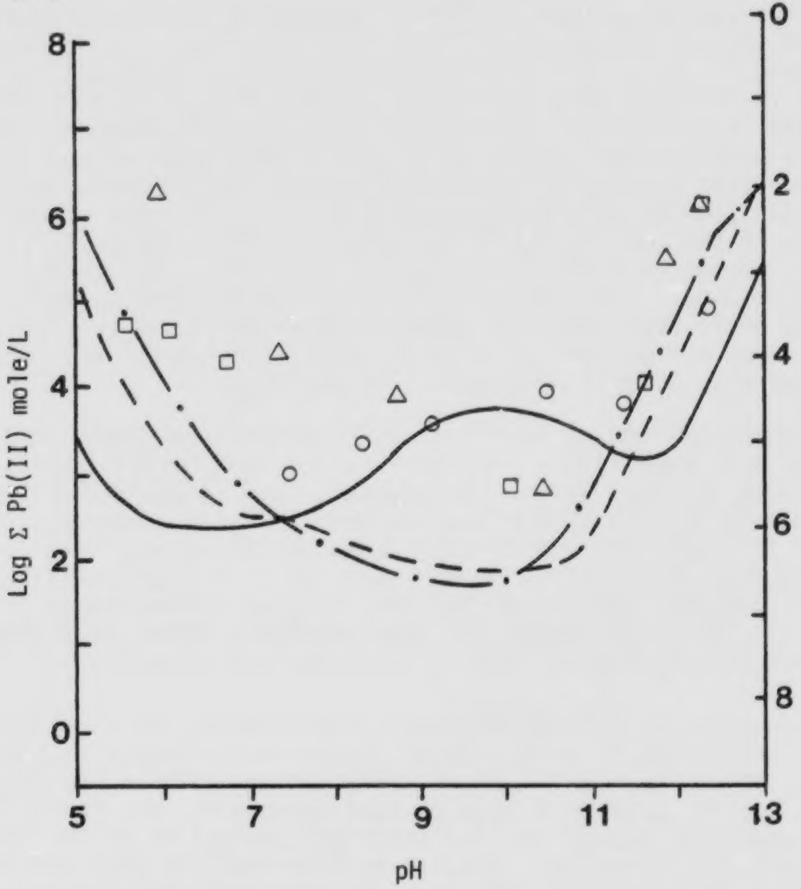


Figure 21. Revised model (I=0.1, 25°C) for log C_t = -3.6 (—— · ——); -2.7 (— —); -1.1 (———). Shown are data from precipitation experiments of Patterson et al (1977) at initial log C_t values of -3.6 (△); -2.7 (□); -1.1 (○) (91).

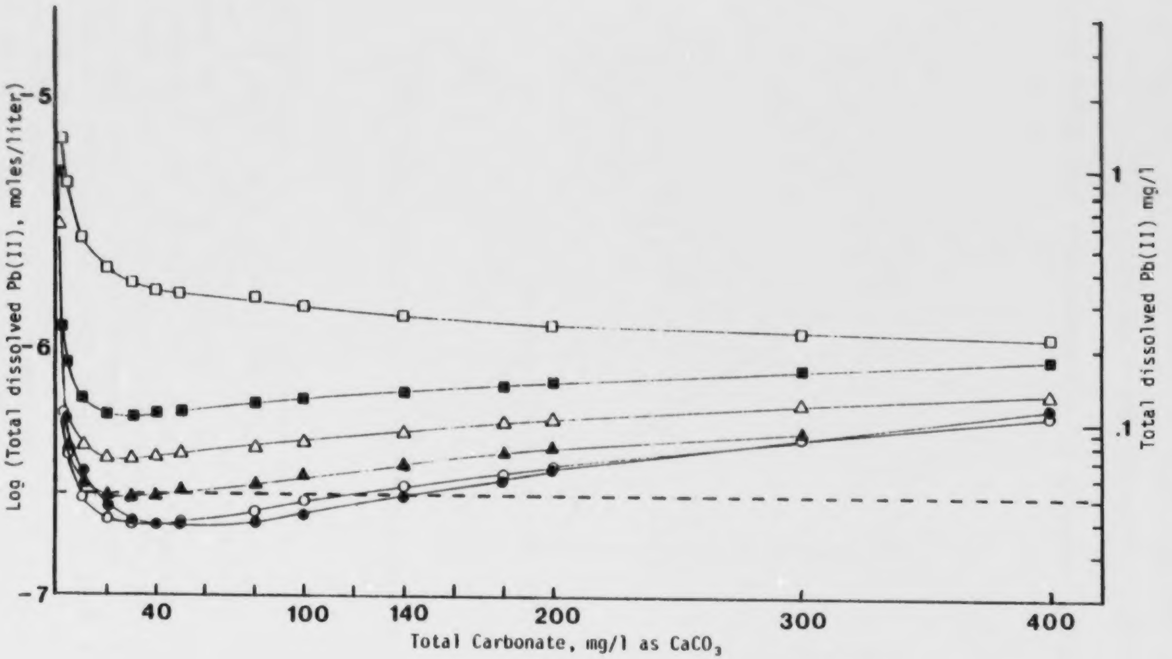


Figure 22. Plot of total dissolved Pb(II) versus C_t at fixed pH (I=0.005, 25°C). Shown are pH = 7.0 (□); 8.0 (■); 8.5 (△); 9.0 (▲); 9.5 (○); and 10.0 (●) (91).

Effects of Temperature--

Results of several investigations have been reported which correlate water temperature with lead corrosion. Using distilled water, Moore determined that the corrosion rate of lead increased exponentially with increasing temperature and developed the relationship:

$$\text{Pb corrosion rate} = 101 \exp(0.01T)$$

where T is temperature (68). Results of his experiment are shown graphically in Figure 23.

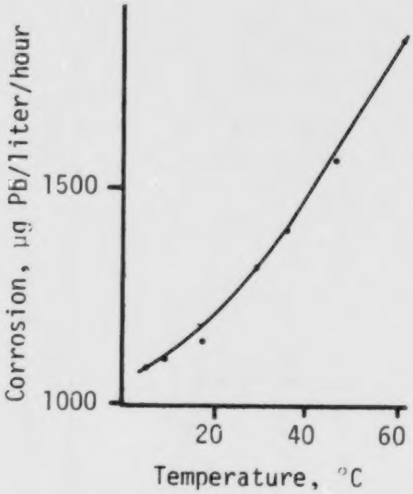


Figure 23. Temperature effects on lead corrosion (68).

Effects of Chlorination--

Schaut attempted to describe the corrosive action of chlorination on lead pipe. From his tests using municipal water with a pH range of 6.8 to 7.2 and an alkalinity of 35-50 mg/ℓ as $CaCO_3$, he concluded that in new lead pipes, the rate of chlorine dissipation is dependent primarily on temperature. Additionally, he observed that when the chlorine was exhausted with increasing temperatures, the water acquired a lead content which approximated the formation of $PbCl_2$. Under all temperature conditions the lead concentration value for new lead pipe was 0.38 ppm. Duplicating his experiment using old lead pipe, Schaut found that the lead concentration in the exposed water did not reach a value of 0.38 ppm even with up to three days contact (90). From the results of his data, Schaut concluded that chlorine contributes its lead equivalent on a percentage basis about equally in old and new lead pipe at maximum potable water temperature, at least for his expermental eight-hour contact period. Additionally, he concluded that the time it takes for water to acquire 0.1 mg/ℓ lead in new lead pipes is approximately 1/4 hour using warm water with a chlorine residual of 0.12 ppm. With cooler water the time required is increased to approximately 1/2 hour (90).

Schaut also investigated the combined effects of water temperature and chlorine concentration and concluded that the combination of chlorine and warm water is more corrosive than warm water alone. In his experiment, Schaut held alkalinity and residual chlorine concentrations constant and varied temperature. Corrosion measurements were made after an eight-hour contact period. Results from this test showed a linear rather than exponential relationship with a doubling of the corrosion rate correlated with a doubling of temperature. Again, Schaut did not provide numerical values.

Effects of Carbon Dioxide--

In a summary report by Slunder and Boyd, results of previous research on the corrosive effects of carbon dioxide content are discussed. Water containing CO_2 in the absence of oxygen has little effect on the corrosion of lead. The extent of corrosion when both CO_2 and oxygen are present is controlled primarily by the concentration of CO_2. Figure 24 is a graphical summary of results reported by several investigators and prepared by Slunder and Boyd which shows the effects of CO_2 content on the corrosion of lead (95). Unfortunately, the specifics of how the CO_2 was added to the water or how the pH was maintained are not presented. As can be seen, when less than 2 mg/ℓ of carbon dioxide is present, corrosion proceeds linearly at an appreciable rate, but at a CO_2 concentration of 60 mg/ℓ, the corrosion rate is much lower. During the tests used to develop this data, a white deposit, probably a basic lead carbonate, was formed with the water having the higher CO_2 concentration (95).

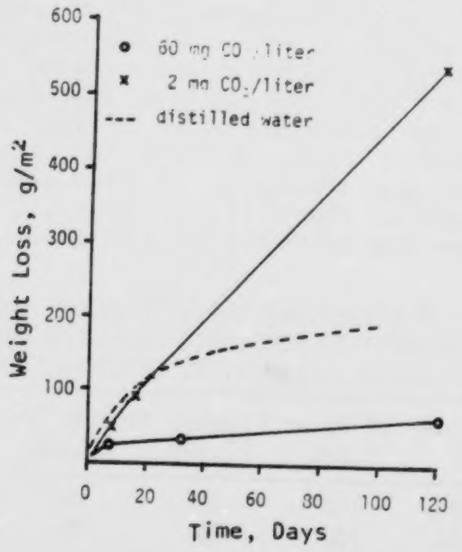


Figure 24. Effects of carbon dioxide content on corrosion of lead (95).

Lead Release from Solder Joints--

Although the primary source of lead in potable waters is thought to occur from lead service lines and lead-lined galvanized pipe used in household plumbing, several studies have been completed to quantify the rate of lead corrosion and water contamination from lead-based solders. Lyon and Lenihan measured the magnitude of lead released from solder joints of copper pipes and found the results to be much higher than expected (65). Their laboratory experiment consisted of a running water test and a static water test using deionized water. In the running water test, water was circulated through a loop constructed of copper tubing with lead-based capillary joints. From the results of the tests, they calculated a mean lead release of 322 μg/fitting/16 hours for the running water test and a mean lead release of 216 μg/fitting/16 hours for the static test. After four to five weeks, a mean lead release of approximately 20 μg/fitting/16 hours was observed from the static tests. These results were favorably compared to measurements taken from capillary joints obtained from a five-year old building which showed a mean lead release of 22 μg/fitting/16 hour period. Lyon and Lenihan concluded that an initial release ranging from 200 to 300 μg/fitting/16 hours can be expected after the first four to five weeks of operation, but that this release will decrease to approximately 20 μg/fitting/16 hours and will be maintained for a long period. It should be noted that these release rates were developed using deionized water. Lyon and Lenihan also noted that the magnitude of the pick-up experienced in the copper tubing was unexpectedly high considering the relatively small surface area of solder exposed. From this observation, it was concluded, through further experiments, that the mechanism for the corrosion process results from galvanic action.

Wong and Berrang also attempted to determine the corrosion or lead pick-up rate of lead-based solders used for joining copper pipes (113). In their experiment, they simulated household copper tubing using 50 feet of one-half inch diameter copper tubing soldered together with 20 soldered joints using 50/50, 60/40, and 95/5 (tin/lead) solder, as well as silver solder. The results of this test for various volumes of water flushed are shown in Table 22. From their experiments, they concluded that an average dissolution rate of 0.4 μg/joint/hour can be expected after one year of service. This value was favorably compared to results obtained from measurements taken from an existing system in a one-year old house. In other experiments, they determined that old lead service pipe will experience a dissolution rate of 30-240 μg/hour and that new lead service pipes will experience a dissolution rate of 480 μg/hour.

TABLE 22. LEAD CONCENTRATIONS (PPB) IN WATER STAGNANT FOR ONE HOUR IN A NEW SIMULATED HOUSEHOLD COPPER PLUMBING SYSTEM
(50 Feet Copper Tubings Joined by 20 Soldered Joints) (113)

	Volume of Water Flushed Through the System (ℓ)				
Solder	80	1,200	12,000	25,000	150,000
50/50	1200	150	96	34	9
60/40	1100	130	49	25	7
95/5	3	2	--	1	--
Silver	2	2	--	1	--
Copper Only	1	2	--	1	--

In his work on heavy metals release from residential plumbling, Rossum (84 ˉ) determined that the typical lead "sweat" fitting provided a clearance of 0.002 to 0.005 inches between the outside of the pipe wall and the inside of the fitting. Thus a ½ inch nominal size type L water tube would have an average of 2.2 square milimeters exposed solder area. Furthermore, the solder alloy was anodic to copper by 0.3 to 0.4 volts in tap water. Rossum reported that lead was released into tap water, regardless of the water quality, from new household plumbing but the length of release varied. Where a calcium carbonate film was able to deposit on the pipe, the current established by the solder-copper galvanic cell was reduced to the extent that within a few weeks the lead release was undetectable. When the film deposition did not occur, the water continued to pick up lead for longer than a year. Rossum also reported that the corrosion inhibition by formation of the film is more effective in flowing than in standing water situations. He also noted that lead pick up may occur from lead impurities used in zinc galvanizing or from brass faucets (typically composed of 6% lead) that may display an exterior of chrome but are seldom plated on the interior walls. The possibility of lead-related health disorders caused by the use of lead solder is documented and problems of excessive lead concentrations occurring in portions of Carroll County, Maryland are presented as a case history in section 6.4.

CORROSION OF ALUMINUM IN THE WATER WORKS INDUSTRY

The use of aluminum is relatively new to the water works industry so its application is presently limited. However, because its corrosive behavior is generally good, aluminum is currently being considered for more extensive use. Typical applications of aluminum in the water works industry include wier gates, storage tanks, reservoir roofs and supports, hot water systems, and water pipelines (9).

Alloys used to manufacture aluminum materials for handling fresh waters include copper, magnesium, silicon, iron, manganese, chromium, zinc, and titanium. Their composition is shown in Table 23. These alloys are sometimes clad with a sacrificial alloy to provide cathodic protection to the core metal. Corrosion induced penetration of an aluminum alloy cladding layer, anodic to the core, will spread laterally after reaching the core. However, as the area of the core is exposed, the resistance of the electrolytic path is increased and penetration of the core may proceed (6).

The corrosion behavior of aluminum is generally good owing to protection afforded by oxide or hydrated oxide films formed on the metal surface. However, corrosion of aluminum in fresh waters can be severe depending on the composition of the water and on the conditions of service.

Several investigators have reported the results of their studies of the effects of fresh waters on the corrosion of aluminum. In general, as aluminum corrodes, most of the surface is usually unaffected while the attack takes the form of small scattered pits. General corrosion or gradual uniform thinning does not occur (38). It has also been observed that, initially, corrosion occurs rapidly through the formation of a large number of pits, but slows considerably in a short period. Porter and Hadden have studied the corrosion of aluminum and have characterized this primary type of corrosion as "nodular pitting" (79). They observed that a mound of insoluble aluminum hydroxide forms on the surface of the exposed aluminum while an acidic liquid builds up underneath, causing the initiation of pits. The rate of corrosion is initially rapid but stabilizes after about two weeks as a cathodic scale forms on the surface of the pit (79).

TABLE 23. COMPOSITIONS OF TYPICAL ALLOYS USED IN FRESH WATERS (6)

Alloy	Cu %	Mg %	Si %	Fe %	Mn %	Cr %	Zn %	Ti %
1C		*	0.23	0.25		*	*	0.01
N3	0.04	*	0.18	0.32	1.18	*	*	0.01
N4	0.10	2.07	0.27	0.27	0.36	*	*	0.01
N5	0.04	3.60	0.17	0.40	0.30	*	*	0.01
N6	0.04	4.94	0.19	0.15	0.31	*	*	0.01
N8	0.03	4.25	0.14	0.24	0.70	0.12	*	0.01
H30	0.04	0.72	0.87	0.27	0.70	*	*	0.01
H19	0.03	0.65	1.04	0.27	0.02	*	*	0.01
H20	0.03	1.01	0.57	0.39	0.12	0.21	0.04	0.05

*Not normally added but may be present at an impurity level.

The predominance of nodular pitting was later confirmed by Davies, and Rowe and Walker (21, 85). Davies investigated the effects of various water quality parameters on exposed aluminum specimens. During his experiments, he observed that bubbles formed on test specimens within 2 to 4 hours after being submerged. Next, white corrosion products developed around the bubble and enveloped it with pit formation beginning within 18 to 24 hours following immersion (21).

Rowe and Walker, investigating the effects of various water quality characteristics on corrosion of aluminum, made similar observations. They also concluded that pitting corrosion was the predominant form of corrosion of aluminum. They observed that the gas bubbles collected on the test specimen soon after being submerged in the test solutions were indicative of the pit sites. At these sites, corrosion mounds began to develop and grew in size with time as gas bubbles continued to rise form the center of the mound. After a longer period, the growth rate of the mounds began to decline. Mechanically removing the corrosion product mound revealed the formation of a pit (85).

Two approaches have been utilized in aluminum corrosion investigations. Porter and Hadden used a qualitative assessment by visual examination and a quantitative assessment by measuring loss of weight, density of pitting, and depth of pitting with all pits on every specimen being measured (79). This basic methodology, with slight modification, was used by others in more recent studies. Rowe and Walker, however, studied the effects of mineral impurities in water on the corrosion of aluminum using an electrical conductance method by passing a known quantity of current through a specimen and measuring the voltage drop. This method does not produce an "absolute" corrosion rate measurement as pits may perforate the specimen. However, a loss of metal by pitting is reflected in the measurement and the method is useful for comparative studies (85).

The effects of various water quality characteristics on the corrosion and pitting of aluminum have been investigated extensively. Characteristics which have been identified as influencing corrosion include pH and total hardness as well as the presence of chlorides, dissolved oxygen, and metal ions. Conditions of service which influence corrosion of aluminum primarily include water velocity, temperature, and time of contact.

Effects of Velocity

Most investigators agree that the corrosion of aluminum occurs more readily in slow moving or stagnant waters than in fast moving waters. In corrosion tests completed by Wright and Godard, it was shown that, in general, as velocity increased corrosion decreased and, from actual field observations, no pitting occurred on aluminum which was exposed to a water velocity of 7 feet/second (115). Other laboratory tests by Godard showed similar results (38). Aluminum specimens immersed in a stagnant water pitted normally while specimens exposed to the same water but at a water velocity of 8 feet/minute showed no pitting. The results of tests by Wright and Godard using Kingston, Ontario tap water are shown in Table 24 (115).

TABLE 24. WATER VELOCITY EFFECTS ON PITTING OF ALUMINUM (115).

	Control Panels in Still Water		Test Panels in Moving Water	
Water Velocity (fpm)	Avg. # of Pits Per Panel	Avg. Max. Pit Depths (μ)	Avg. # of Pits Per Panel	Avg. Max. Pit Depths (μ)
1	95	206	244	148
2	360	156	145	107
3	126	176	26	79
4	174	227	58	90
5	119	236	26	50
6	142	156	15	35
7	347	133	50	29
8	59	155	0	0
10	85	188	0	0

Excessively high velocities may, however, enhance corrosion. From field studies conducted by Godard, it was observed that at water velocities of approximately 20 feet/second, turbulence occurred, especially at fittings, resulting in pitting (38).

Effects of Temperature

Godard also investigated the effects of water temperature on the incident and growth of pits on aluminum (38). The results of his investigation are shown in Figure 25. From Figure 25 it is shown that as the temperature rises the probability of pitting increases and the pitting rate decreases. In other experiments, Godard measured the current flow from machined pit specimens exposed to various water temperatures (38). The results of that experiment are shown in Figure 26. Godard found that the current flow reached a maximum at around 40°C and dropped off quickly as the temperature increased. At 70°C corrosion, as indicated from the current flow, was below that observed at room temperature. In other experiments, Godard found that the current flow decreased linearly over the entire temperature range and no maximum was observed. From his experiments, he concluded that at above 40°C, the service life of aluminum equipment would increase with increasing temperature (38). Consequently, aluminum is well suited for domestic hot water system applications.

Godard also determined that in the pitting of aluminum, the rate of penetration follows a rapidly decreasing rate curve that approximates a cube root function. From examination of laboratory pitting data, he concluded that the maximum pit depths (d) were proportional to the cube root of time (t) and he described the rate of penetration by the expression

$$d = Kt^{1/3}$$

where K is a function of the alloy and water characteristics. Actual time is measured from the initiation of the pit. This expression has been verified using actual field observations (38).

Water Quality Effects

As early as 1920, Seligman and Williams investigated the effects of various combinations of chlorides, sulfates, carbonates, and bicarbonates on the corrosive behavior of aluminum. From the results of their investigation, they concluded that pitting of aluminum is due to the simultaneous presence of chloride and bicarbonate in water provided there is free access of oxygen to the system (79).

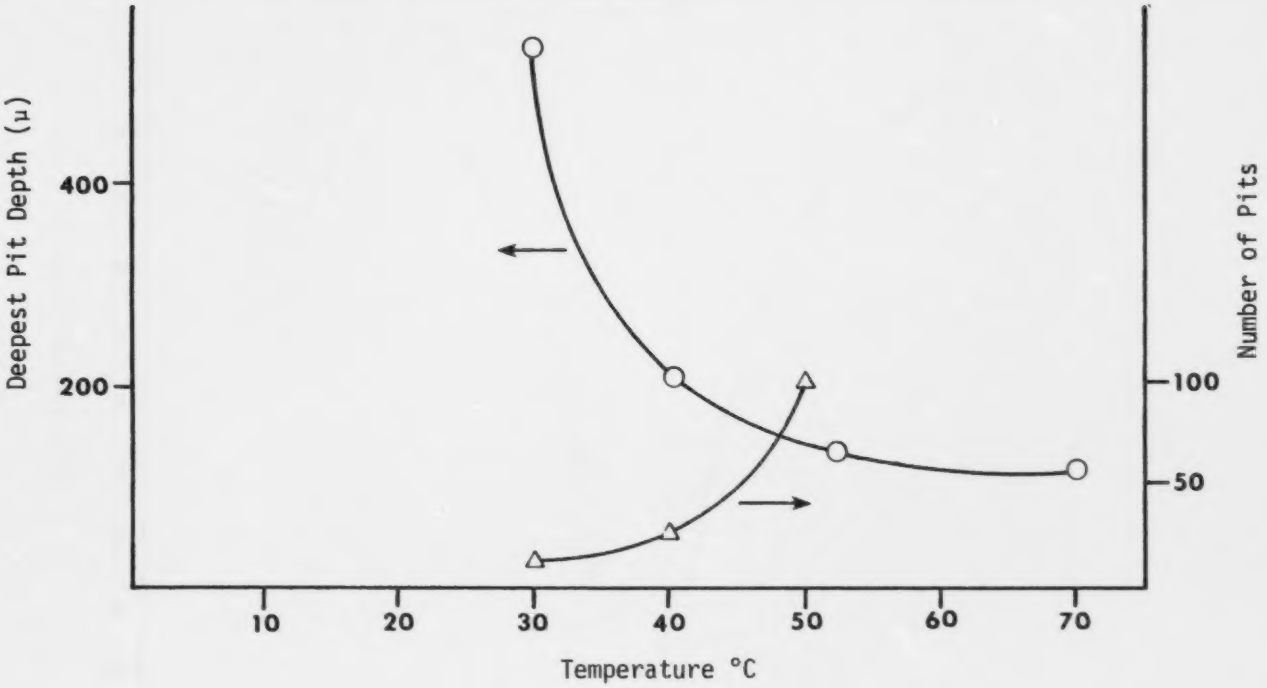


Figure 25. Temperature effects on pitting of aluminum (38).

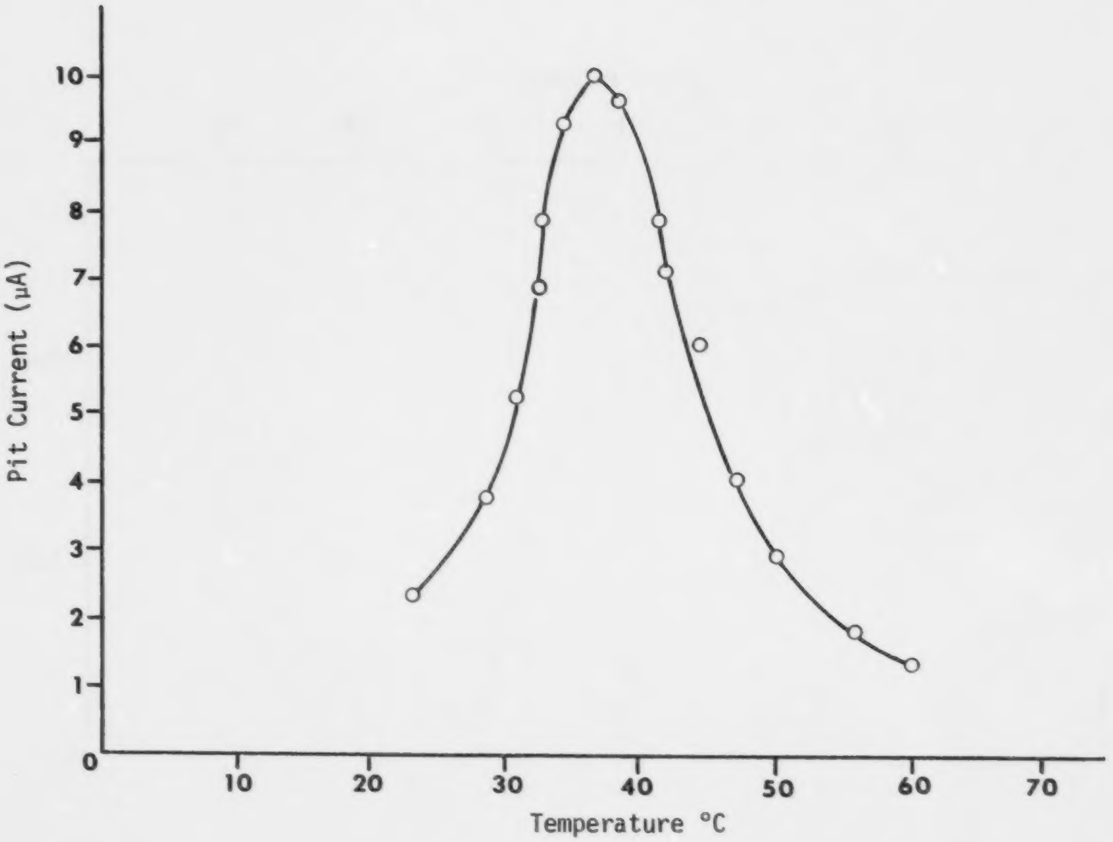


Figure 26. Temperature effects on pit current (38).

In later experiments, Porter and Hadden isolated several water quality characteristics to determine their singular effect on corrosion of aluminum. These characteristics included copper ion, dissolved oxygen, and hardness. In general, they determined that in the absence of copper ions, dissolved oxygen, and hardness nodular type pitting is prevented. They concluded that the characteristics which are necessary for the initiation of pitting include temporary hardness, chlorides, copper, and dissolved oxygen. It was also found that the water composition is more influenced on the corrosion of aluminum than is the composition of the aluminum specimen (79).

Porter and Hadden also investigated the effects of these parameters on the maintenance of pits. These tests were preformed by transferring specimens to other controlled aqueous environments after pitting was initiated. It was found that dissolved oxygen was essential for maintenance of pitting as pitting ceased in de-aerated waters. The removal or absence of copper ion, however, did not prevent the maintenance of pitting, but the rate of pitting was slowed.

In an effort to establish typical pitting curves, Godard compared the constituents of seventeen fresh waters with the resulting corrosion (38). He concluded that no simple correlation exists and, because of the wide variation in the composition of waters, it would be difficult to establish the aggressiveness of waters to aluminum from tables alone. He did conclude from his data, however, that hard waters are generally more aggressive to aluminum than soft waters. The partial composition and pitting data for fresh waters compiled by Godard are shown in Table 25 (38).

TABLE 25. PARTIAL COMPOSITIONS AND PITTING DATA FOR SEVENTEEN FRESH WATERS (In Increasing Order of Pitting Corrosivity) (38)

Order	Test No.	Weeks to 40 Mils.	Location	pH	Hardness p.p.m.	Copper p.p.m.
1	8	953	Shawinigan South, Que.	7.1	73	0.04
2	7	453	Shawinigan, Que.	7.4	18	0.04
3	12	207	Crofton, B.C.	6.7	27	0.024
4	6	205	Hamilton Bay, Ont.	7.1	205	0.003
5	6		Kingston, Ont.	7.9	160	0.005
6	5	175	Credit Valley, Ont.	7.1	0	0.028
7	4	147	Columbia River, B.C.	7.5	72	0.017
8	16	83	Canyon Meadows, Alta.	7.9	169	0.005
9	14	46	Regal Golf Course, Calgary, Alta.	8.1	331	0.007
10	1	25	N. Sask. River,Drayton Vly., Alta.	8.1	267	0.11
11	13	23	Peterborough, Ont.	7.5	86	0.012
12	15	17	R.G.May Golf Course,Calgary, Alta.	7.9	218	0.002
13	22	8	Billingham Beck, England	8.7	443	0.011
14	24	6	Jasper, Alta.	8.2	195	0.007
15	2	6	Lethbridge, Alta.	7.9	228	0.017
16	9	4.4	South Saskatchewan River, Sask.	7.6	206	0.04
17	10	2.6	Mossbank, Sask.	7.8	555	0.005

Davies investigated the effects of sodium chloride, calcium carbonate, and dissolved copper on the pitting of aluminum under controlled conditions using water which he composed in the laboratory. All testing was performed under static conditions (21).

In general, Davies observed that pitting occurs more readily in waters containing calcium bicarbonate, chloride, dissolved oxygen, and copper salts. To further characterize the effects of these parameters on the corrosion of aluminum, Davies investigated both the singular effects and the combined effects of two and three constituents.

For the one constituent test, Davies prepared solutions of 10, 30, and 50 ppm of chloride ion in the absence of other ions, and solutions of 10, 80, and 150 ppm calcium ion, as calcium bicarbonate, in the absence of other ions. In each solution prepared, Davies exposed aluminum specimens and observed the pitting or corrosion characteristics. For waters containing chloride ions only, a negligible attack was observed. Even after six months of exposure, the appearance of the test speicmen had not sufficiently changed.

In tests with water containing calcium bicarbonate only, little corrosion was visible. However, specimens showed a slight tarnish which became more pronounced with increasing calcium ion concentration.

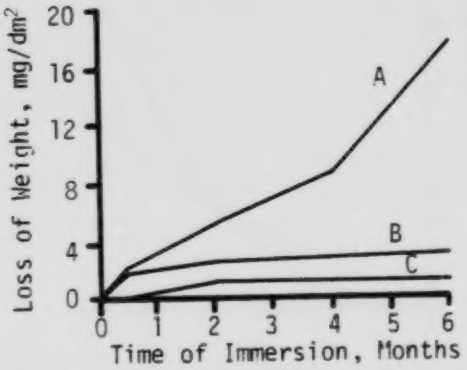
For experiments containing two constituents, Davies prepared test solutions by combining chloride and copper ions, calcium and copper ions, and chloride and calcium ions. He observed a slight weight loss in specimens in tests with waters containing both chloride and copper ions. Also, he observed the formation of a few nodular type shallow pits which increased in number and depth with increasing copper content.

Results of tests using solutions containing both calcium bicarbonate and copper ions showed a negligible weight loss in test specimens. The aluminum surface was essentially unchanged in appearance except for a slight dulling.

When the chloride and calcium bicarbonate ions were present in the absence of copper, Davies observed a slight weight loss in the test specimens. Additionally, only slight changes in the appearance of the specimens were observed.

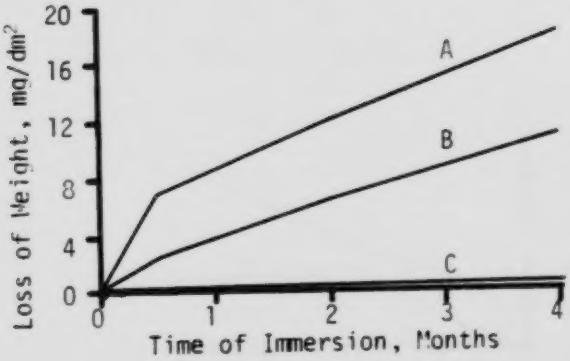
In experiments where all three constituents were present, a very pronounced corrosion effect in the form of nodular pitting was observed. The results of Davies experiments are shown graphically in Figures 27 through 29. In waters where the chloride content was equal to or in excess of the calcium ion content, there was both a general attack as well as a localized attack. The general attack was in the form of a brown stain which was noticeable after two weeks and became more pronounced with time.

Davies compared his results using the laboratory solutions with tests using tap water to determine the effects of the presence of copper ions. The results of these tests are shown in Figure 30. No weight loss was observed with tap water which did not contain copper ions. However, when copper ions



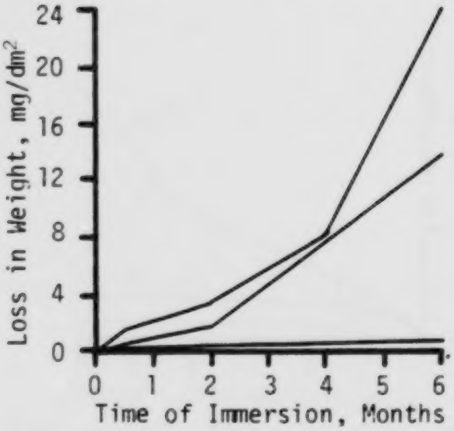
A. $Cl^- = 30$ ppm, $Ca^{++} = 10$ ppm, $Cu^{++} = 0.2$ ppm
B. $Cl^- = 30$ ppm, $Cu^{++} = 0.2$ ppm
C. $Ca^{++} = 10$ ppm, $Cu^{++} = 0.2$ ppm

Figure 27. Weight loss of aluminum in various water qualities (21).



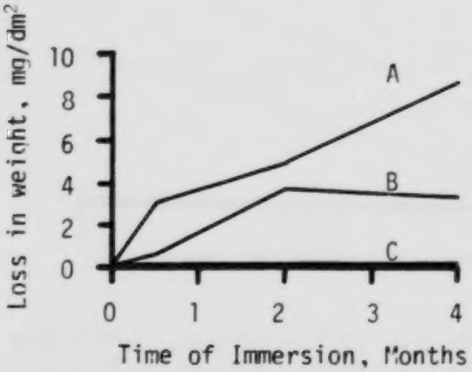
A. $Cl^- = 50$ ppm, $Ca^{++} = 80$ ppm, $Cu^{++} = 0.2$ ppm
B. $Cl^- = 50$ ppm, $Ca^{++} = 80$ ppm, $Cu^{++} = 0.06$ ppm
C. $Cl^- = 50$ ppm, $Ca^{++} = 80$ ppm

Figure 28. Effects of copper on weight loss of aluminum (21).



A. Cl^- = 10 ppm, Ca^{++} = 10 ppm, Cu^{++} = 0.2 ppm
B. Cl^- = 10 ppm, Ca^{++} = 10 ppm, Cu^{++} = 0.06 ppm
C. Cl^- = 10 ppm, Ca^{++} = 10 ppm

Figure 29. Effect of low calcium content on weight loss of aluminum (21).

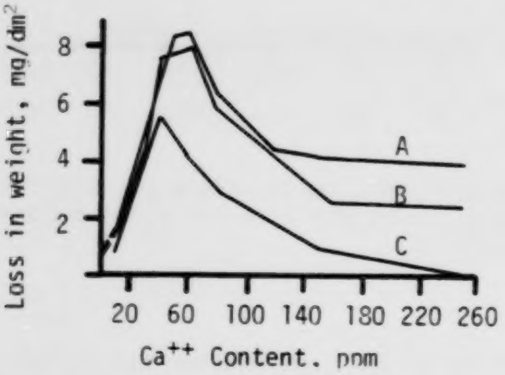


A. Tap water + Cu^{++} @ 0.2 ppm
B. Tap water + Cu^{++} @ 0.06 ppm
C. Tap water only

Figure 30. Weight loss of aluminum in tap water (21).

were added to the tap water, similar corrosion results occurred as with the laboratory test solution.

Because of the significant influence of the presence of copper ions on the corrosion of the test specimens, Davies further studied the effects of chloride and calcium ions by varying the chloride-calcium ion ratio and holding the copper ion constant at 0.2 ppm. The results of these experiments after submerging the specimens for two weeks are shown in Figure 31. The results indicate that with a two-week exposure period, a maximum weight loss is observed with a calcium ion concentrate of approximately 50 ppm. Additionally, weight losses increased with increasing chloride ion concentrations. For solutions containing less than 10 ppm calcium ion concentrations, pits were very small and not of the nodular type. At calcium ion concentrations above 150 ppm, almost no pitting was observed, but the specimens were covered with a whitish deposit. It is important to note that the above observations were made from experimental results obtained after exposure of specimens for a two-week period only.



A. $Cl^- = 50$ ppm, $Cu^{++} = 0.2$ ppm
B. $Cl^- = 30$ ppm, $Cu^{++} = 0.2$ ppm
C. $Cl^- = 10$ ppm, $Cu^{++} = 0.2$ ppm

Figure 31. Effect of Ca^{++}/Cl^- ratio on weight loss (21).

Bell also investigated the effects of calcium carbonate on corrosion of aluminum in waters containing chloride and copper. The results of his tests did not provide any evidence of a maximum in the severity of corrosion at any particular calcium or calcium carbonate concentration as previously reported by Davies (5). Therefore, Bell conducted additional tests to identify the apparent discrepancy.

In his experiments, Bell exposed aluminum test specimens in water containing various concentrations of calcium carbonate ranging from 50 to 600 ppm. The chloride ion content was held at 50 ppm and the dissolved copper ion content was held at 0.2 ppm. The pH ranged from 6.5 to 7.4, with the higher values being recorded at the conclusion of the tests. The results of his experiments for various lengths of exposure are shown in Figure 32, and the maximum pit depths observed are shown in Table 26.

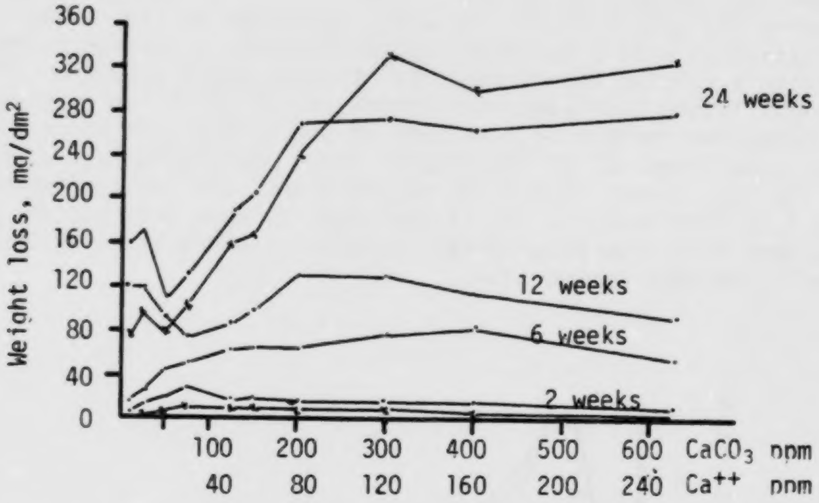


Figure 32. Effect of calcium carbonate on weight loss of aluminum specimens (solutions also contained 50 ppm chloride and 0.2 ppm copper) (5).

TABLE 26. EFFECT OF $CaCO_3$ ON MAXIMUM PIT DEPTHS (mm)
(Solutions also Contained 50 ppm Cl^- and 0.2 ppm Cu) (5)

Time		2 Weeks		6 Weeks	12 Weeks	24 Weeks	
Material		A	B	B	B	A	B
$CaCO_3$ p.p.m.	Ca p.p.m.						
10	(4)	< 0.02	0.08	0.15	0.13	0.22	0.27
25	(10)	0.11	< 0.02	0.19	0.18	0.22	0.28
50	(20)	0.18	< 0.02	0.28	0.26	0.48	0.25
75	(30)	0.24	< 0.02	0.32	0.41	0.50	0.37
125	(50)	0.24	0.24	0.37	0.44	0.64	0.55
150	(60)	0.17	0.22	0.42	0.48	E	0.51
200	(80)	0.19	0.39	0.32	0.47	E	0.71
300	(120)	E	0.30	0.55	0.61	0.28	0.52
400	(160)	0.12	0.22	0.42	0.42	E	0.67
625	(250)	0.11	E	0.31	E	0.48	0.61

E = attack on the edges only

The results of Bell's studies indicate that a maximum weight loss is dependent on the time of exposure for various calcium carbonate concentrations. For example, for specimens immersed for two weeks, the maximum weight loss occurred in the solution containing 75 ppm calcium carbonate. For those specimens immersed for 12 to 24 weeks, the maximum weight loss was least for waters containing 75 ppm calcium carbonate.

From his tests, Bell observed that when the calcium carbonate content was less than the chloride ion content, corrosion proceeded slowly with a slight general type of attack in the first two to six weeks. After six weeks, a film formed on the surface of the specimen and the corrosion rate increased sharply with the formation of numerous tiny mounds of corrosion product each with a pin point underneath. These pits increased in size with time of exposure. In tests where the calcium carbonate and chloride ions were approximately equal in concentrations, the rate of weight loss decreased with time as a result of film formation and very few pits were formed.

In waters containing more than 125 ppm calcium carbonate, nodular type pitting developed. It was also observed that with increasing calcium carbonate concentrations, the corrosion product mounds increased in size but decreased in number. Additionally, it was observed that these pits tended to form on the edges of the specimen with increased calcium carbonate content.

For waters containing 125 to 150 ppm calcium carbonate, Bell observed that a thick white amorphous film containing very little calcium carbonate was deposited on the specimen. At calcium carbonate concentrations of 625 ppm, no white film was produced and deposits between the pits consisted only of calcium carbonate (5).

From his experiments, Bell concluded that the relative loss of weight of aluminum specimens is dependent on the period of immersion, and for periods greater than 12 weeks, corrosion is least in waters with approximately equal concentrations of chloride and calcium carbonate. He also states that corrosion of aluminum is also dependent on sulfate content and pH and that measuring chloride, calcium carbonate, and copper concentrations is not sufficient to adequately characterize the corrosion phenomena of aluminum (5).

In their experiments, Rowe and Walker investigated the effects of chloride, sulfate, bicarbonate, calcium, and copper on the corrosion of aluminum. They observed that the corrosion rate was low in aerated distilled water. Additionally, no substantial increase in corrosion rate was observed when either chloride, sulfate, bicarbonate, or calcium were added to the distilled water at concentrations as high as 300 ppm, or copper ion up to 2 ppm. The addition of a combination of any two of these constituents also did not produce a substantial increase in corrosion rate. However, the combination of chloride, bicarbonate, and copper ions in the presence of air did produce a significant corrosion rate increase (85).

With these initial results, the additional testing by Rowe and Walker focused on the combined effects of chloride, bicarbonate, and copper. They concluded that a near maximum contribution to corrosion of aluminum occurs at an ion concentration of approximately 300 ppm for chloride and bicarbonate and approximately 2 ppm for copper. The results of these tests are shown in Figure 33 (85).

It should also be noted that while copper has been cited as the most aggressive metal to aluminum, other metal ions such as tin and nickel (79) and mercury (38) have been found to have detrimental effects on the corrosion of aluminum.

Davies conducted corrosion tests on anodized aluminum specimens with oxide films ranging in thickness from 0.05 to 1.35 μ (21). These specimens were immersed in a water containing 40 ppm chloride ion, 40 ppm calcium ion, and 0.2 ppm copper ion for a period of two weeks. This water is known to be aggressive to aluminum and gives rise to pit formation. Some specimens were sealed while others were not.

Results of tests on the sealed specimens indicated that corrosion rate is decreased even for specimens anodized for only a few seconds. One specimen with an oxide thickness of 0.4 μ, which was formed after 50 seconds of anodizing, was found to be immune to corrosion. However, Davies states that if tested longer, pitting would probably occur. The same results were not observed for unsealed specimens and pitting occurred. Davies concluded that for anodizing to be effective, the specimen must be sealed (21).

Booth et al conducted studies to obtain data in an effort to predict the service life of aluminum, primarily pipelines exposed to fresh waters (6). They concluded that, in general, severe pitting of aluminum pipelines, short of perforation, will not significantly affect their service life. From pipe sections which were severely pitted, the materials tensile strength was only slightly affected. The pipe bursting strength was affected, but not to the point that would constitute a failure. Failure would occur first by perforation. Booth et al also reported that for small to moderate diameter aluminum water pipes, the hydraulic efficiency will be reduced approximately one percent per annum over the first ten years of service life (6).

ASBESTOS-CEMENT PIPE PERFORMANCE IN THE WATER WORKS INDUSTRY

Asbestos-cement pipe was first manufactured in Europe in 1913 and was introduced in the U.S. in 1929 (98). Approximately one-third of all water distribution pipe currently being sold in the U.S. is manufactured of asbestos-cement. Since its introduction approximately 200,000 miles of asbestos-cement pipe has been placed into service for transporting potable waters (41).

Asbestos-cement pipe is composed of 15 to 20 percent asbestos fiber, 48 to 51 percent cement, and 32 to 34 percent silica. The cement portion is either Portland cement, Portland blast furnace slag, cement, or Portland pozzolena cement (98).

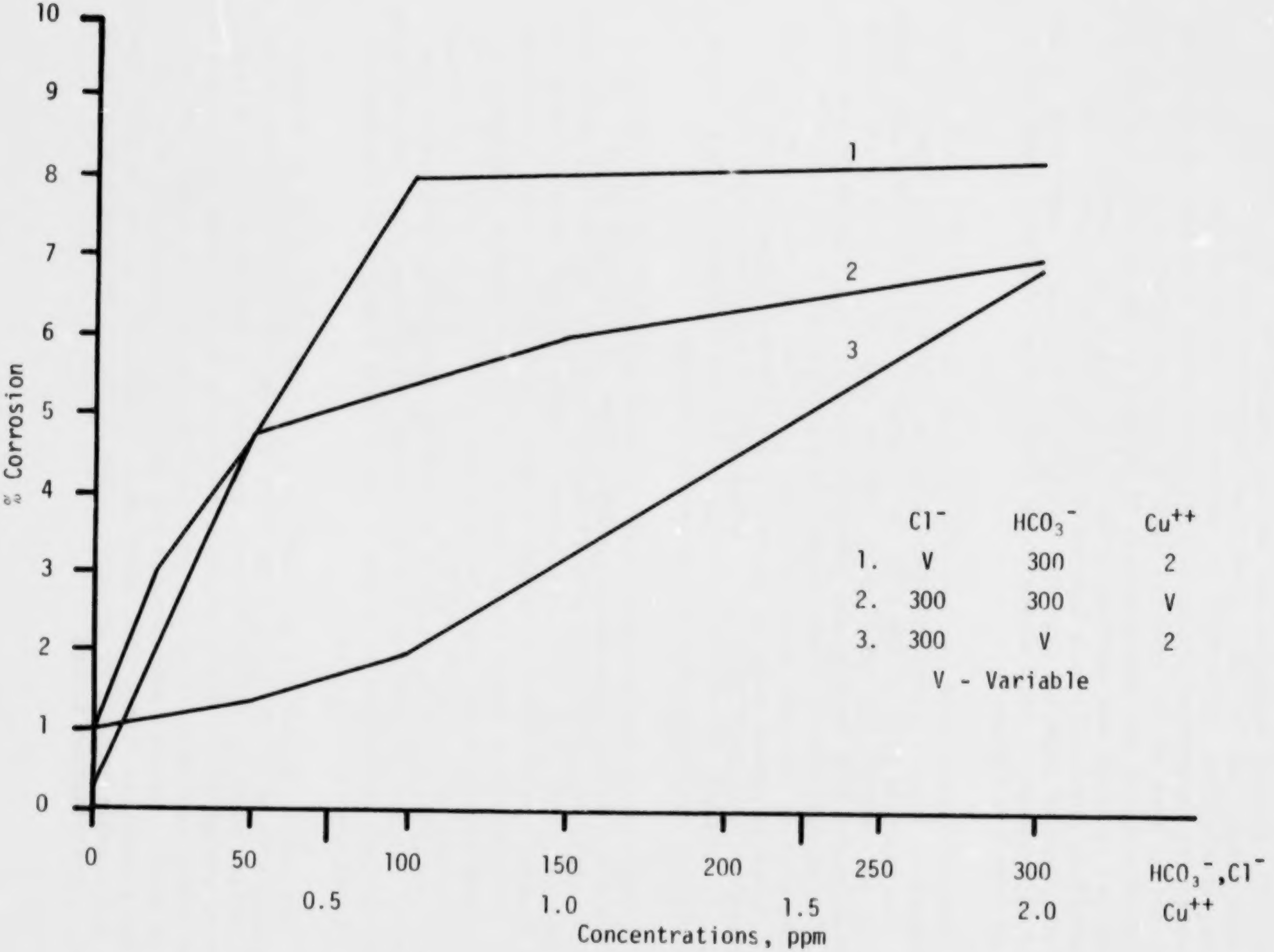


Figure 33. Corrosion of aluminum after 22 hours of exposure in solution containing chloride, bicarbonate, and copper (85).

Asbestos is a generic term representing a number of fibrous silicate minerals. These minerals vary in their metallic content, fiber diameter, flexibility, tensile strength, and surface properties. Six asbestos minerals have been identified for their commercial importance and are chrysotile, amosite, crocidolite, anthophyllite, amphiboles, and actinolete. Chrysotile referes to the serpentine [$Mg_6Si_4O_{10}(OH)_8$] variety of asbestos and comprises 80 percent or more of the asbestos used in asbestos-cement pipe (41). Chrysotile accounts for approximately 95 percent of the world's asbestos production and is mined and quarried primarily in Quebec and Vermont (88). It is identified physically as a tubular or hollow fibrous material. The remaining type of asbestos used for manufacture of potable water pipe is the crocidolite variety. This mineral is a fibrous blue or bluish green silicate of iron and sodium.

Asbestos-cement pipe is available in sizes ranging from 4 to 36 inches in diameter. Type II asbestos-cement pipe is autoclaved while Type I is not. The interior base of the pipe is polished during production and, therefore, is very smooth and requires no interior coating. During installation, asbestos-cement pipe lengths are joined by special couplings which are also made of asbestos-cement. These couplings are machined to fit over the machined ends of the pipe using two flexible O-rings to ensure a watertight seal. Asbestos-cement pipe can be easily drilled and tapped to provide additional service when necessary. Advantages of asbestos-cement pipe include an immunity to electrolysis due to its non-conductor status, and a low hydraulic resistance due to its smooth interior.

Several investigations have been initiated to determine if asbestos minerals are released from asbestos-cement pipe into potable water. In general, these investigations have attempted to correlate various water quality conditions and pipe ages with asbestos fiber releases or occurrences in potable waters after passing through a specified length of asbestos-cement pipe. The results of these investigations will be discussed subsequently. First, however, it is important to note the difficulty in conducting these investigations and obtaining meaningful results. Therefore, a brief discussion of the problems encountered in attempting to qualify or quantify the potential release of asbestos fibers from asbestos-cement pipe into drinking waters follows to provide an appreciation or understanding of the reported results and their limitations.

Asbestos is ubiquitous and asbestos fibers of one variety or another are present in soils throughout the U.S. The most frequent occurrences of near surface asbestos fibers in soils are found in the western and Atlantic seaboard states (51). These asbestos fibers are also present in our nation's water supply sources as they are leached from the soils by runoff and recharge water. Natural wind erosion and earth disturbances will also act to transport asbestos fibers into water ways. Therefore, it can be aniticipated that appreciable amounts of asbestos fiber may exist in potable water as it enters a distribution system.

To determine if asbestos fibers are released from asbestos-cement pipe in potable water distribution systems, it is necessary to quantify incremental changes in asbestos concentrations or fiber counts as the water enters and passes through the pipe. Observed incremental changes in asbestos concentrations or counts, however, do not necessarily indicate a release from the asbestos-cement pipe. Increases in fibers or fiber concentrations may result by contamination from the surrounding serpentine soil which remains in the pipe following construction or repairs.

In one study, conducted by the Vermont Department of Health, Sargent reported that asbestos fibers can appear in potable water distribution systems which do not use asbestos-cement pipe (88). The objective of their study was to compare various sources and to determine if asbestos fibers were picked up in distribution systems. To eliminate the effect of the ubiquitous nature of asbestos and its possible presence in source water, the investigators took samples of both the source and the distribution system and compared the results of the analysis. The results showed that in 17 out of 23 systems initially sampled, the number of asbestos fibers increased from source to distribution, while in six systems it actually decreased.

Incremental increases may also result from drilling and tapping operations when the interior surface of the pipe is disturbed. Although the release of asbestos fibers via drilling and tapping is directly associated with the use of asbestos-cement pipe, measured incremental increases observed during field or laboratory studies should not be construed as normal release of asbestos fibers from the smooth interior surface. Therefore, during such investigations, any drilling and tapping or other pipe disturbances must be identified for corrections.

The analytical procedures used to determine asbestos fiber release in asbestos-cement pipes is presented in Section 5. However, it should be noted that current techniques are based on microscopic quantification may be specific to a certain type of fiber and may not report fiber size. While the effect of ingested asbestos fibers on health has not been determined, it is assumed that the type and size may be important fiber parameters (51). Also, these techniques are often imprecise and generally valid to within an order of magnitude.

Causes of Asbestos Fiber Release

Several investigations have been conducted to ascertain that asbestos-cement pipe does undergo deterioration resulting in the release of asbestos-cement fibers in potable water systems. Other more recent investigations have been initiated in an attempt to identify and quantify the various characteristics which affect asbestos-cement pipe performance. The results of most studies reported to date indicate that structural deterioration is usually negligible even with apparently high asbestos fiber counts, although a measurable decrease in pipe thickness may occur. Primary characteristics identified for examination include water quality, detention or pipe-water exposure time, pipe age, and installation practices.

Hallenbeck et al investigated the effects of pipe age on the release of asbestos fibers (41). For this study, paired samples were taken from 15 public water systems in Northeast Illinois. The transmission electron microscope analysis technique was used to detect and count chrysotile fibers. Paired samples were collected for comparison and were representative of before and after passing through asbestos-cement pipe. The field data collected and the results of this study are shown in Table 27.

As can be observed, a wide variety of water quality characteristics were investigated. Consequently, the authors performed statistical tests on the before and after sample pairs. Although some increases occurred, the authors concluded that no statistical significant release of chrysotile fibers was observed. In some analyses, it was found that the fiber counts increased. From fiber length measurements, it was determined that this increase was probably due to breakage in fiber as the fibers were generally shorter in the after exposure samples.

Tracy also investigated the effects of pipe aging on the release of asbestos fibers from asbestos-cement pipe (104). In this investigation, water quality samples for pH, hardness, and alkalinity were collected from various locations in the distribution systems and changes were observed. Asbestos-cement pipe sections of various ages were selected for this study from three communities in Vermont which were Brattleboro, South Shaftsbury, and South Burlington. Water quality observations were continued over nearly a four-year period to identify any effects of pipe aging. Water quality sampling and analytical results from this study are shown in Table 28.

In Table 28 it is shown that significant increases in pH, alkalinity, and hardness were observed from samples collected from the Brattelboro and South Shaftsbury distribution systems which were approximately five years old. Samples collected from these same facilities after they had been in service for approximately nine years showed less significant changes. Additionally, Tracy observed from the results of samples taken from the nine-year-old South Burlington system that only slight changes in water quality occurred in portions of the distribution system where circulation was good as compared to dead-end sections where circulation is minimal. From the results of this study, Tracy concluded the asbestos-cement pipe may stabilize with age and become more resistant to water quality characteristics (104).

Buelow et al investigated the behavior of asbestos-cement pipe under various water quality conditions (9). The specific objective of their study was to determine if asbestos-cement pipe would be attacked and asbestos fibers released under the various conditions. Their approach was to select ten water supply systems throughout the U.S. which utilized asbestos-cement pipe and which had various water quality characteristics with respect to pH, calcium hardness, and alkalinity. Pipe sections from most of the systems were visually inspected and the samples were analyzed using the electron microscope technique. The results of their study were reported as a correlation between a water quality aggressive index, calculated from the value of the water quality parameters listed above, and the incremental increase in asbestos fibers observed from samples selected.

The aggressive index used for the Buelow et al study follows that procedure identified by AWWA Standard C400-77 which establishes criteria for

TABLE 27. FIELD DATA STUDY - DATA COLLECTED AND RESULTS (41)

WATER SYSTEM	PIPE AGE (Years)	PIPE LENGTH (Feet)	WATER QUALITY		MASS OF CHRYSOTILE FIBERS OBSERVED 10^{-5}g/Grid Square	
			pH	Aggressive Index	Before	After
Groundwater Systems:						
Westmont	0.5	200	7.1	11.2	0.15	0.92
Lisle	1.0	3,000	7.7	12.5	0.13	0.44
Hoffman Estates	18.0	3,700	8.2	12.7	0.28	0
Rolling Meadows	20.0	4,400	7.5	12.2	1.06	0
York Center	27.0	1,100	7.7	12.8	0.03	0.27
Lake Michigan Systems:						
Bannockburn	1.0	1,300	8.4	12.4	0.53	3.78
Bradley Road	14.0	1,000	8.4	12.4	5.97	0.41
Zion-Benton	18.0	10,000	8.1	12.1	0.41	1.25
Waukegan	19.0	600	DATA NOT AVAILABLE		17.21	4.71
Zion	26.0	1,150	8.1	12.1	0.28	0.34
Midlothian	27.0	1,500	8.2	12.2	1.27	1.05
Blue Island	30.0	3,248	8.2	12.2	29.90	6.63
Brook Field	35.0	40,000	8.2	12.2	0.92	0.28
Glenview	37.0	1,500	7.6	11.5	0.39	0.82
Highland Park	40.0	275	7.9	11.8	0.24	0.10

TABLE 28. EFFECTS OF PIPE AGING (104)

BRATTLEBORO
(Installed in 1941)

	Center of Village			N. 1.5 mi on Cement-Asbestos Pipe			N. 2 mi at Dead End		
	9/45	8/46	4/49	9/45	8/46	4/49	4/45	8/46	4/49
pH	7.2	7.2	7.5	9.2	9.1	8.2	9.9	9.6	8.6
Hardness	30.0	31.0	46.0	48.0	48.0	40.0	57.0	51.0	42.0
Total Alkalinity	30.0	24.0	24.0	41.0	36.0	27.0	55.0	50.0	30.0

SOUTH SHAFTSBURY
(Installed in 1940)

	Reservoir			N. 0.6 mi on Cement-Asbestos Pipe			N.W. 1.2 mi at Dead End		
	10/45	9/46	'49 ave.	10/45	9/46	5/49	10/45	9/46	5/49
pH	6.6	7.3	7.2	6.8	7.8	8.3	9.6	8.4	9.5
Hardness	24.0	29.0	32.0	26.0	29.0	24.0	45.0	50.0	40.0
Total Alkalinity	12.0	20.0		15.0	22.0	12.0	35.0	41.0	26.0

SOUTH BURLINGTON
(Installed in 1936; extended in 1948)

	City Line		E. 1.1 mi on Cement-Asbestos Pipe		E. 1.9 mi at Dead End		E. 3.1 mi at New Dead End After 1948
	11/45	8/49	11/45	8/49	11/45	8/49	8/49
pH	7.0	7.4	7.2	7.4	8.2	7.5	8.2
Hardness	54.0	46.0	54.0	50.0	54.0	74.0	72.0
Total Alkalinity	37.0	41.0	41.0	42.0	44.0	45.0	48.0

determining the quality of water that can be transported through asbestos-cement pipe without any adverse structural effects. Although this parameter is often presented in asbestos-cement studies, it is not always accurate in predicting a tendency to release fibers or to allow $Ca(OH)_2$ leaching (34). The aggressive index (AI) is calculated as:

$$\text{Aggressive Index} = \text{pH} + \log\,[AH]$$

where,

pH = index of acidity or alkalinity in standard pH units
A = total alkalinity in mg/ℓ as $CaCO_3$
H = calcium hardness in mg/ℓ as $CaCO_3$

Values greater than 12.0 identify non-aggressive water; values between 10.0 and 11.9 identify moderately aggressive water; and values less than 10.0 identify highly aggressive waters.

Three of the systems investigated had a water quality aggressive index in excess of 12.0 and are, therefore, considered non-aggressive. Samples collected from these systems were, in general, free of asbestos fibers. Only two samples collected from the three systems which had passed through asbestos-cement pipe had asbestos fiber counts which were statistically significant. The highest value reported was 0.3 million fibers per liter (MFL). In this analysis, a fiber count of 0.2 MFL was also indentified in the water source or at the treatment facility.

Two of the water systems investigated had a water quality aggressive index between 10.0 and 11.9 and are considered moderately aggressive. The first system reported had an aggressive index of 11.56 and the second had an aggressive index of 10.48. Only two samples collected from the first system had fiber counts which were statistically significant. Both values were 0.2 MFL. A third sample taken from the well pump had an asbestos fiber count of 0.1 MFL.

In the second system which had a moderately aggressive water (aggressive index = 10.43), changes in water quality with respect to pH, calcium hardness, and alkalinity were also monitored at two sampling locations. It was observed that pH and calcium concentrations increased as the water passed through the asbestos-cement pipe. This increase indicates that calcium hydroxide or other calcium products in the cement binder were being dissolved resulting in an increase in pH and calcium concentrations in the water, and demonstrates that water aggressive to asbestos-cement pipe will continue to increase in pH and calcium with time of exposure as the water seeks its calcium saturation level (9). In this system significant asbestos fiber counts ranging up to 4.6 MFL were observed. However, because of the large fluctuations in the number of fibers found in various samples, the authors explained the high fiber counts as originating from pipe tapping in the sample collection area.

Five of the ten systems investigated had a water quality aggressive index less than 10.0 and are considered highly aggressive to asbestos-cement pipes. For these five systems surveyed, the aggressive index ranged from 5.34 to 9.51. From the results of this investigation, several important observations were made. In general, water samples taken from the system showed that pH and the aggressive index increased as the aggressive water passed through the asbestos-cement pipe indicating that the asbestos-cement pipe serves a source of pH adjustment. With only one exception, high fiber counts were measured in these water systems having highly aggressive waters as was anticipated. In these tests pipe sections were removed for inspection and pipe deterioration and loosened fibers were apparent where high fiber counts were observed. In one test where asbestos-cement pipe was exposed to a water having an aggressive index of 8.74, the pipe inspection showed that the cement binder had been dissolved to a depth of 1/8 inch.

In another test by Buelow et al, asbestos-cement pipe was exposed to a water having an aggressive index of 6.0 to 7.5 and a pH ranging from 4.5 to 6.0. Although a high asbestos fiber count was expected, very few were actually observed. Additionally, a visual inspection showed little deterioration, but instead the presence of an iron rust-like coating. It is suspected that this iron rust-like coating actually provides a protective coating against pipe deterioration from aggressive water. Susequent laboratory testing confirmed this speculation (9). A summary of the results of the field test completed by Buelow et al is shown in Table 29.

The Environmental Protection Agency Drinking Water Research Division also conducted laboratory studies to investigate the performance of asbestos-cement pipe under various water quality conditions (9). In the initial testing, full lengths of four-inch and six-inch diameter pipes were used in an effort to simulate actual conditions and minimize problems associated with laboratory scale down. However, during the testing, water quality conditions were difficult to maintain as a drift in pH and alkalinity concentrations were observed owing to the exposure of the water supply source to carbon dioxide in the atmosphere. Despite the problems encountered, some interesting qualitative results were observed. For example, it was observed that iron, dissolved in the water from some of the experimental equipment, precipitated and provided a protective coating on the asbestos-cement pipe and halted calcium leaching. From this initial experimental test it was also verified that drilling and tapping of asbestos-cement pipe will generally result in increased fiber counts in water and this increase can be significant (9).

Because of the difficulties in controlling water quality conditions in this initial experimental test, a laboratory scale coupon test experiment was performed. The objective of this study was to investigate the effects of controllable water quality conditions on asbestos-cement pipe deterioration. This study included the use of chemical additives as a corrosion control strategy. A summary of the water quality conditions used in the experiments and general observations made are shown in Table 30.

A comparison between Tests 1 and 2 indicated that the addition of zinc orthophosphate to a concentration of 0.3 to 0.5 mg/ℓ provided protection for the asbestos-cement pipe. It was observed that zinc was gradually depleted but the phosphate was not.

Experimental Tests 3 and 4 were companion tests to further study the potential of zinc orthophosphate for protection at a lower pH and lower aggressive index. The results indicated that the use of zinc orthophosphate at a lower pH or aggressive index was not as effective for preventing

TABLE 29. SUMMARY OF FIELD DATA COLLECTED BY BUELOW ET AL (9)

System	Initial Aggressive Index	pH	Alkalinity mg/ℓ as $CaCO_3$	Calcium Hardness mg/ℓ as $CaCO_3$	Consistently Quantifiable Fibers	Pipe Wall Deteriorated as Determined by Inspection	Significant Observations
1	5.34	5.2	1.0	1.4	Yes	Yes	Water pH and A.I. increased as water passed through A/C pipe; A/C pipe served as source for pH adjustment.
2	5.67	4.8	3.0	2.5	Yes	Yes	High fiber counts were observed in water samples; observation on pipe section removed confirmed pipe deterioration.
3	7.46	6.0	4.0	7.5	No	No	Asbestos fibers were generally absent from water samples; observations of pipe section suggested that an iron rust-like coating provided protection from attack of this highly aggressive water.
4	8.74	7.1	89.0	0.5	Yes	Yes	High fiber counts were observed in water samples; observation on pipe section removed confirmed pipe deterioration.
5	9.51	7.2	14.0	14.5	Yes	Yes	Water pH increased with exposure time to A/C pipe.

Continued

TABLE 29 (Continued)

System	Initial Aggressive Index	pH	Alkalinity mg/ℓ as $CaCO_3$	Calcium Hardness mg/ℓ as $CaCO_3$	Consistently Quantifiable Fibers	Pipe Wall Deteriorated as Determined by Inspection	Significant Observations
6	10.48	8.3	20.0	7.5	Yes	N.I.*	Large fluctuations in water sample fiber counts indicated that pipe tapping may be responsible for the presence of some asbestos fibers.
7	11.56	7.5	88.0	82.0	No	N.I.	Water samples collected were generally free of asbestos fibers as is expected from this moderately aggressive water.
8	12.54	7.8	220.0	250.0	No	N.I.	Water samples collected were free of asbestos fibers.
9	12.74	9.4	50.0	44.0	No	N.I.	Water samples collected were free of asbestos fibers.

*N.I. = Not Inspected

TABLE 30. WATER QUALITY CONDITIONS AND GENERAL OBSERVATIONS FOR SMALL SCALE EXPERIMENTS (9)

Experiment No.	pH	Calcium mg/ℓ as $CaCO_3$	Total Alkalinity mg/ℓ as $CaCO_3$	Aggressive Index	Corrosion Control Method	General Observations
1	8.2	6	20	10.28	None	Alkalinity and calcium concentrations increased significantly during experiment; coupon was softened.
2	8.2	6	20	10.28	Zinc Orthophosphate	Alkalinity and calcium concentrations increased slightly during test; coupon retained hard surface; light gray coating on the pipe surface was observed.
3	7.0	10	20	9.30	None	Alkalinity and calcium concentrations increased; coupon was softened.
4	7.0	10	20	9.30	Zinc Orthophosphate	Alkalinity and calcium concentrations increased; coupon was softened.
5	8.2	6	20	10.28	Zinc Chloride	Alkalinity and calcium concentrations increased slightly; coupon retained hard survace.
6	7.5	145	125	11.76	None	(Unsaturated with respect to $CaCO_3$); coupon was softened.
7	7.9	145	125	12.16	Slightly Positive Langlier Index	Coupon retained hard and clean surface.
8	9.0	25	40	12.00	$CaCO_3$ Saturation	Coupon was slightly softened.

asbestos-cement pipe deterioration. It does, however, appear to offer some protection.

Experiment 5 was performed to determine if zinc alone, not phosphate, was repsonsible for providing protection. Comparison of the results between Experiments 2 and 5 verified that previous observation.

Experiments 6 and 7 were performed to demonstrate the performance of $CaCO_3$ as a protection mechanism under conditions of saturation and unsaturation. For these experiments, pH was used as the controlling variable for $CaCO_3$ saturation. From Experiment 6, it was shown that the asbestos-cement pipe was attacked by a water which was unsaturated or unstable with respect to $CaCO_3$, although the aggressive index was high. Alternatively, Experiment 7 showed that a water which was saturated with respect to $CaCO_3$ did not attack the asbestos-cement pipe.

Experiment 8 was a test of the aggressiveness of water at the point of saturation. This condition is between the conditions tested in Experiment 6 and 7. Results of this test, as expected, showed a slight softenting of the coupon.

Subsequent investigations have developed an asbestos-cement pipe protection model to alleviate problems of improper predictions based on the A.I. by considering the overall water chemistry, and not just the $CaCO_3$ saturation (34).

Organic Release from Asbestos-Cement Pipe

The appearance of significant concentrations of tetrachloroethylene in potable water has recently been associated with the use of lined asbestos-cement pipe. In an investigation performed by the Environmental Protection Agency, pipe sections of lined and unlined asbestos-cement pipe were immersed in a beaker of water and water samples were analyzed at the start, one hour, six hours, and 24 hours later. In these experiments no detectable level of tetrachloroethylene was observed in samples taken from the unlined pipe beaker. However, in the experiments using the lined asbestos-cement, the following results were observed (55):

TETRACHLOROETHYLENE CONCENTRATION ($\mu g/\ell$)

Exposure Time	Test 1	Test 2
0 hour	Not Detectable	Not Detectable
1 hour	8	14
6 hours	25	25
24 hours	41	20

Water quality samples have been collected from the field where lined asbestos-cement pipe sections have been installed. Tetrachloroethylene concentration as high as 2508 $\mu g/\ell$ were observed from samples collected at Brenton Point Park in Newport, Rhode Island, in October 1977 (55). Samples collected from a new lined asbestos-cement service line in Newport showed a level of 56.7 µg/ℓ (1). Results showing levels in excess of 30 µg/ℓ have recently been reported in Vermont (55).

In an effort to identify the source of tetrachloroethylene, the Environmental Protection Agency has investigated the techniques used in fabrication and installation of asbestos-cement pipe. Tetrachloroethylene is used to clean the internal surface of asbestos-cement pipe prior to application of the liner. Therefore, it is concluded that the quantity or concentration of tetrachloroethylene which is released to the water is at least paritally dependent on the durability and integrity of the lining (55). It should be noted that this process has been stopped, and no pipes manufactured with the process are being sold.

CONCRETE PIPE

Concrete pipe was first used for transporting potable waters in 1910, but widespread use of concrete pipe did not occur until after 1930. Concrete pipe is composed of Portland cement, sand and gravel aggregates, water, and reinforcing steel. Three types of concrete water pipe are available and are classified in accordance with the method of reinforcement. These three types are steel cylinder, not prestressed; steel cylinder, prestressed; and noncylinder, not prestressed.

Concrete pipe for transporting potable waters can be either prefabricated at a central plant or manufactured on site. Concrete pipe can be constructed in any size, but pipe diameters generally range form 12 to 96 inches. Concrete pipe sizes up to 180 inches in diameter have been produced for water systems.

Concrete pipes are usually coated or lined internally with a specified mixture of mortar or concrete. If the pipe will be exposed to aggressive water, an internal coating of cutback asphalt is sometimes spray applied. Concrete pipe sections are joined with a modified bell and spigot joint, and a gasket is used to ensure a watertight fit. The space between the pipe and the two joining pipes is filled with mortar (98).

Concrete pipe has been used extensively for water distribution with pipe being in service for 50 years or more in some locations. The suitability and acceptance of concrete pipe for water mains is well established, but concrete pipe can be attacked in some circumstances by aggressive waters or soil conditions (94). Additional coatings are applied in such cases.

Although it is not strictly a concrete because aggregate is not present, Portland cement coatings can be applied to protect cast iron or steel water pipe on either the water or soil side or both. The cement protects the underlying from corrosion by the aggressive environments. The coating which may be applied by centrifugal casting, trowelling, or spraying ranges in thickness from 0.25 to greater than one inch. The cement coatings are subject to the same types of attack as concrete pipe. A disadvantage of cement coatings is the sensitivity to damage by mechanical or thermal shock.

However, small cracks in cold-water pipes may be automatically plugged with a reaction product of corrosion combining with alkaline products leached from the cement.

A series of investigations during the 1950's were based on visual inspection and surface layer analysis of cement lined or concrete pipe (29, 30). The samples were removed from various water supply service lines and the following conclusions regarding their deterioration resulted:

1) Concrete pressure pipe is only slightly affected by even aggressive water over service periods of 25 years or longer.

2) As seen in the cement-to-calcium oxide ratios shown in Table 31, the removal of calcium oxide from concrete pipes is limited to a surface layer less than 0.25 inches deep.

TABLE 31. CEMENT-TO-CALCIUM OXIDE RATIO
(With Respect to Depth from Pipe Surface) (29)

Depth (inches) City	Inside 0.075	Next 0.150	Next 0.150	Next 0.150	Next 0.150	Remaining
Portland ME (3 yrs/service)	1.77	1.54	1.53	1.51	1.54	1.56
Milton PA (9 yrs/service)	1.76	1.71	1.59	1.58	1.63	1.60
St. Petersburg FL (25 yrs/service)	2.24	1.59	1.50	1.48	1.48	1.47

3) Reduction in CaO content is not the controlling factor in determination of the service life of the pipes.

4) The limiting factor in leaching CaO from concrete pipe may be the formation of a surface deposit of magnesium silicate and calcium carbonate.

5) There appeared to be no difference in the amount of CaO leached from either fine or coarse ground cement.

Dissolution of calcium compounds by aggressive waters are the primary concern on the water side of concrete pipe, but attack by soil conditions is also important, primarily to maintain structural integrity. Some soils will react with the cement in the concrete or mortar. Alkali soils contain sulfate compounds that cause gradual deterioration of concrete made with standard Portland cement but there are formulations of sulfate-resistant cement for use in these areas (4). Acid soils may contain sufficient acid to react with concrete pipe or mortar. Cut-back asphalt, coal applied tar, or coal tar epoxy may be used to coat the exterior of the concrete pipe to protect it from the acid content of the soil (4).

PLASTIC PIPE

Commercial plastic pipe was first introduced in 1930 in Germany and later in 1940 in the United States. The first type of plastic pipe commercially available was polyvinyl chloride (PVC). Large-scale production of plastic pipe, however, did not begin until after 1948 with the production of polyethylene (PE) for application in various water uses. Plastic pipe was initially used in the water works industry for service lines and household plumbing, and most pipe was two inches in diameter or smaller. However, with continued development, a larger plastic pipe is now available and is used for water distribution mains, service lines, and in-plant piping systems.

The use of plastic pipe and fittings is steadily increasing in potable water systems as well as in other more corrosive environments. Several varieties of plastics are used in making pipe. Characteristics and physical properties of plastics can vary within a chemical group as well as from one group to another. The two major classifications of plastics are thermoplastics and thermosets, and both are used in the manufacture of pipe. However, thermoplastics are the material of choice for potable water systems. Thermoplastics soften with heating and reharden with cooling which allows them to be extruded or molded into components for piping. Thermosets are permanently shaped during the manufacture of an end product and cannot be softened or changed by reheating.

Total use of thermoplastic piping in 1978 exceeded 3 billion pounds which was approximately one-third of the footage of all piping (69). Approximately two-thirds of the thermoplastic piping manufactured in the United States is used for water supply and distribution, including community and municipal systems and for drain, waste, and vent piping (116). The principal thermoplastic materials in piping are as follows:

1) polyvinyl chloride including chlorinated polyvinyl chloride,

2) polyethylene,

3) acrylonitrile-butadiene-styrene,

4) polybutylene,

5) polypropylene,

6) cellulose acetate integrate, and

7) styrene-rubber plastics.

Other thermoplastics can also be made into piping for special applications. The fist four plastics above account for approximately 95 percent of the total plastic pipe and fittings produced (33). Polyvinyl chloride, polyethylene, and polybutylene are the plastics most often used for potable water supplies. Short descriptions of the various plastics are given below. Typical physical properites of the major thermoplastics are summarized in Table 32.

Polyvinyl Chloride (PVC)

PVC is a good example of the variations that can occur within a chemical group. The properties of the thermoplastic depend on the combinations of PVC resins with various types of stabilizers, lubricants, fillers, pigments, processing aids, and plasticizers. The PVC resin is the major portion of the materials and determines the basic characteristics of the thermoplastic but the amounts and types of additives influence such properties as rigidity, flexibility, strength, chemical resistance, and temperature resistance.

Rigid PVC or Type I PVC are the strongest PVC materials because they contain no plasticizers and the minimum of compounding materials. Type II PVC materials are made by adding modifiers or other resins and are easier to extrude or mold, have higher impact strengths, lower temperature resistance and lower hydrostatic design stresses, and are less rigid and chemically resistant. Chlorinated polyvinyl chloride (CPVC) is a Type IV PVC made by the post chlorination of PVC. CPVC is similar to Type I PVC but has a higher temperature resistance. Both Type I PVC and CPVC materials have a hydrostatic design stress of 2000 psi at 75°F. Type I is useful up to 140°F while CPVC is useful to 210°F.

The long-term strength and higher stiffness of PVC makes it the most widely used thermoplastic for both pressure and non-pressure application. PVC is used in water mains, water services, drain, waste, and vent, sewerage and drainage, well casing, and communication ducts. The higher temperature resistance of CPVC makes it applicable for hot/cold water and industrial piping.

Polyethylene

Polyethylene is a polyolefin formed by the polymerization of the ethylene. Polyethylene plastics are waxy materials that have a very high chemical resistance. The resistance of polyethylenes is such that piping structures must be joined by thermal or compression fittings rather than solvent cements or adhesives. Carbon black may be added to polyethylene to screen ultraviolet radiation.

Polyethylene compounds are classified by the density of the natural resins. Type I materials are low density, relatively soft, flexible, and have low heat resistance. Type I materials have a low hoop stress of 400 psi with water at 73°F and are seldom used for pipe. When used for pipe, Type I is used for low head piping or open-end piping; therefore, it is seldom used in potable water systems. Type II polyethylenes are medium density compounds. These materials are harder, more rigid, resistant to higher temperatures, and more resistant to stress cracking. The high density polyethylenes, Type III, have maximum hardness, rigidity, tensile strength, chemical

TABLE 32. TYPICAL PHYSICAL PROPERTIES OF MAJOR THERMOPLASTIC PIPING MATERIALS (69)

Property @ 75°F	ASTM Test No.	ABS		PVC		CPVC	PE		PB	PP	PVDF
		I	II	I	II		II	III			
Specific Gravity	D-792	1.04	1.08	1.40	1.36	1.54	0.94	0.95	0.92	0.92	1.76
Tensile Strength psi (10^3)	D-638	4.5	7.0	8.0	7.0	8.0	2.4	3.2	4.2	5.0	7.0
Tensile Modulus psi (10^5)	D-638	3.0	3.4	4.1	3.6	4.2	1.2	1.3	0.55	2.0	2.2
Impact Strength, Izod ft-lbs/inch notch	D-256	6	4	1	6	1.5	>10	>10	>10	2	3.8
Coeff. of Linear Expansion in/in-F (10^5)	D-696	5.5	6.0	3.0	5.0	3.5	9.0	9.0	7.2	4.3	7.0
Thermal Conductivity Btu-in/hr-ft-F	C-177	1.35	1.35	1.1	1.3	1.0	2.9	3.2	1.5	1.2	1.5
Specific Heat Btu/lb-F	-	0.32	0.34	0.25	0.23	0.20	0.54	0.55	0.45	0.45	0.29
Approx. Operating Limit*											
F, nonpressure	-	180	180	150	130	210	130	160	210	200	300
F, pressure	-	160	160	130	110	180	120	140	180	150	280

*Exact operating limit may vary for each particular commercial plastic material (consult manufacturer). Effects of environment should also be considered.

resistance, and temperature resistance. Their hydrostatic design stress for water at 73°F is 630 psi.

Many water utilitites use polyethylene for cold water distribution and service lines. The pipe most often used is two inches or less. The toughness, low flexural modules, and chemical resistance are important considerations in water service connections. It is most often used outside buildings.

Polybutylene

Polybutylene is also a polyolefin. Its use in potable water systems has been expanding considerably. Polybutylene is similar to low density polyethylene in rigidity, but its strength is greater than that of high density polyethylene. However, its significant characteristic is its ability to retain strength with increasing temperature. Polybutylene has a hydrostatic design stress of 1000 psi for water at 73°F and 500 psi for water at 180°F. Polybutylene is used for hot and cold water distribution, water distribution and service, gas distribution and services, and industrial piping. The flexibility of polybutylene makes it useful for main-to-meter water service tubing and well piping. It also protects against hot water backup into cold water systems. Polybutylene is used inside buildings for hot and cold water lines.

Acrylonitrile-Butadiene-Styrene (ABS)

ABS plastics are manufactured from the three monomers from which the class name is derived. ABS piping materials are similar to Type II PVC but vary according to the ratios of the component monomers. Acrylonitrile provides rigidity, strength, hardness, and chemical resistance. Butadiene makes the plastic tougher. Styrene contributes gloss, rigidity, and easier processing.

ABS plastic piping is relatively rigid with good impact shrength. The hydrostatic design stresses for water at 73°F range from 800 to 1600 psi. ABS plastic piping may be used up to 180°F in non-pressure applications. ABS may be used to convey potable water but its most common use is for drain, waste, and vent.

Polypropylene

Polypropylene is another polyolefin but it is not as widely used in potable water systems as polyethylene or polybutylene. It is similar to high density polyethylene, but it is more rigid and temperature resistant. Its good chemical resistance makes it more useful in environments harsher than potable water systems.

Deterioration and Releases from Plastic Piping

Very little direct information exists on the corrosion or, more appropriately, deterioration of thermoplastic materials in potable water systems. One of the significant features of thermoplastics is the good chemical resistance of the compounds; this feature was responsible for many of the early applications of thermoplastics in handling highly corrosive materials. The ability of thermoplastics to withstand harsh chemical environments has received most of the attention directed toward the corrosion of these materials. Most testing has concentrated on physical properties. Consequently, little attention has been focused on thermoplastics in such relatively mild environments as potable water systems. A recent study by the National Bureau of Standards acknowledges the widespread acceptance of themoplastic piping for residential plumbing and the absence of recent reports of failures due to chemical attack or environmental stress cracking. This trend suggests that these failures have ceased to be of significant concern in the use of thermoplastics in residential and related applications (116).

There are two general types of chemical attack on plastic pipe (33). One is a solubility reaction where a chemical is removed from the plastic, contaminating the fluid flowing in the pipe. The leached chemical may be non-reacted components, reaction products, or impurities, but their leaching should not significantly alter the physical properties of the pipe. From steric considerations, the leachable components probably lie close to the pipe surface. The second type of chemical attack is where a polymer or base resin molecule is altered by chain breakage, cross linkage, oxidation, or substitution reactions. In these cases, the properties of the plastic may be irreversibly altered, and the fluid flowing in the pipe may or may not become contaminated. The chemical resistance of plastics may vary within differenct grades of the same type as a result of minor chemical or process differences. In general, a better chemical resistance exists when smaller amounts of compounding additives are used. Most plastic pipe compounds conforming to ASTM specifications use a minimum amount of compounding ingredients, although CAB plastics may use chemically susceptible monomeric plasticizers while PVC Type II uses chemically resistive impact modifiers.

Compared to metals and other construction materials, thermoplastics are generally superior in resisting corrosion. Thermoplastics are not subject to electrochemical corrosion because they are not conductors. Such electrochemical effects as galvanic corrosion do not occur with thermoplastics. As examples, soils which are corrosive to metal pipes or in which stray currents are present do not present problems for buried thermoplastic pipe. The resistance of thermoplastics alleviate the need for such measures as cathodic protection and special coatings.

Inorganics do not present significant threats to thermoplastics; most are not affected by acid and alkaline salts. Thermoplastics are resistant to polar active compounds such as acids, bases, and brines. The thermoplastics are resistant to chemical concentrations in normal household operations or potable systems. Although most plastics absorb water to a slight extent, water does not produce corrosion or other types of deterioration. Under some circumstances direct chemical attack by inorganic species such as oxygen, chlorine, other strong oxidizers, very strong acids or alkalis, and ultraviolet radiation may lead to deterioration of the plastics. Some thermoplastics such as PVC have additives such as carbon black to protect against ultraviolet rays which might otherwise degrade the long chain structure upon long duration exposure (72). However, it is unlikely that chemical attack by these types of species would be significant in potable water systems because they would have to be present in such large concentrations that hazards greater than thermoplastic deterioration would exist.

Since thermoplastics are organic materials, they are subject to deterioration by reaction with some organic compounds, primarily via a solution mechanism. The solvent cementing of plastic pipe is based on solution. The effect of organic species on thermoplastics varies with the organic compounds and plastics. For example, PVC is not affected by most esters and ketones but cellulose acetate butyrate readily dissolves in most esters and ketones. Aromatic species are the most likely class of compounds to attack thermoplastic piping. However, if organic compounds are present in sufficient concentrations to deteriorate thermoplastic they present other more significant and immediate problems from a water quality standpoint.

Environmental stress cracking is another form of degradation that may affect thermoplastics in piping systems. The process is believed to occur when a surface active agent such as an alcohol or detergent acts on surface flows in a stressed or strained plastic (69). Some degree of stress concentration, particularly at joints or fittings, might arise from 1) forced alignment of pipes and fittings, 2) building settlement, 3) lumber shrinkage, 4) thermal expansion or contraction, or 5) long-term dimensional changes (116). A chemical test for potable water pipe and fittings has been suggested by the Federal Construction Council of the Building Research Advisory Board, but this test as well as others suffers from 1) uncertainties in the representativeness of the conditions and 2) effects of exposure duration (116).

Although the data are limited, there have been several studies of thermoplastic pipe deterioration in potable water and simulated environments (72, 93, 99, 101, 102, 110). Tiedeman conducted studies to determine the possible effects of plastic pipe on the safety, quality, and palatability of water (101, 102). He conducted extraction tests to determine the aggressiveness of several water systems on various thermoplastic pipes. The results of the tests showed that no undesirable substances were extracted from the plastic pipe, with the exception of three samples that were known to contain substances which might be extractable. A typical set of results are shown in Table 33. With a pH 9.6 in test waters, 0.34 ppm lead was extracted from a plastic pipe in which a lead compound was used as a stabilizer. Lowering the pH to 1.0 by adding hydrochloric acid extracted 2.0 ppm lead. However, the results were obtained under extreme conditions of temperature, exposure duration, and area of plastic exposed per unit volume of test waters (101).

Over the course of a three-year study, it was found that the most aggressive potable water was a relatively soft water with the pH adjusted to 5 by adding carbon dioxide (102). This water extracted lead compounds from specially prepared test plastics. However, the extraction results were negative for all specimens of plastic pipe recommended for use with potable water. A Soviet study of the extraction of lead from PVC pipe materials also confirmed that lead stabilizing compounds could be leached from the PVC in potable water supplies (93). However, these results were on Soviet pipes which do not apply in this country. Changes in plastic pipe exposed to

TABLE 33. TYPICAL EXTRACTION TEST RESULTS* (101)

Plastic Pipe No.	Color ppm	Turbidity ppm	Odor	Taste‡	Total Solids		Alkalinity		pH	Fe ppm	Al ppm	NO_2 ppm	NO_3 ppm	Cl ppm	SO_4 ppm	Total Hardness ppm	Residual Cl ppm	DO ppm
					Residual ppm	Dissolved ppm	Phenolphthalein ppm	Total ppm										
none	6	3	0	0	152	156	10	36	9.70	0.1	0.003	0.02	0.02	10.9	53.9	95	0.3	11.2
C†	6	5	0	0	168	172	11	35	9.70	0.1	0.003	0.03	0.15	10.9	54.7	108	0.02	8.4
120	8	5	0	med	164	164	10	40	9.65	0.1	0.003	trace	0.08	12.4	54.2	110	0.01	9.0
160	6	7	0	m	172	176	10	39	9.65	0.25	0.014	0.01	0.04	11.5	56.2	97	0.01	9.6
170	6	6	0	med	176	172	9	36	9.60	0.1	0.003	0.04	0.05	11.8	55.2	102	0.01	9.8
none	0	5	0	0	176	176	23	62	9.90	0	0	0.01	0.02	10.9	64.3	114	0.15	10.8
C†	0	5	0	0	176	192	20	59	9.70	0	0	0.0	0.04	10.9	62.9	114	0.01	6.6
110	0	5	6.7	med	184	184	21	60	9.85	0.2	0	0.1	0.02	10.2	64.3	116	0	8.6
150	0	5	0	med	188	176	20	58	9.85	trace	0	0.1	0.02	12.1	71.0	118	0.01	9.0
180	0	7	2	med	184	182	20	58	9.75	0	0	0.2	0.02	12.1	63.4	114	0	8.2
none	0	1		0	144	144	24	54	9.50	0.1	0	0.002	0.12	10.9	48.2	90	0.8	9.8
C†	0	2		0	160	128	12	50	9.45	trace	0	0.004	0.20	10.9	41.3	92	0	9.2
200	2	2		med	168	140	8	42	9.22	0.1	0	0.004	0.28	10.3	49.4	90	0	9.0
210	0	3	17	med	168	144	6	46	9.20	0.1	0	0.005	0.16	10.7	34.1	91	0	9.0
220	0	1		med	160	148	24	68	9.50	trace	0	0.005	0.40	10.7	44.2	92	0.3	9.2

* [illegible] contact time, [illegible] extraction tests [illegible] ran for lead [illegible] were all negative.
† Control [illegible] material [illegible]
‡ [illegible] musty.

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outdoor conditions or buried in soil at pH 2.0 and held at 35°C were slight after exposures of one year. Discoloration was the principal change in both exposures (102).

One concern is the extraction or leaching of organic species from pipe cements into water supplies. A recent study indicated that it is possible to leach such solvents as 2-butanone (MEK) and tetrahydrofuran (THF) from PVC pipe cement (110). Two sets of water samples were collected six and eight months after PVC pipe installation and usage in a laboratory. About 40 gallons of water were used daily in the laboratory. The water temperature was about 21°C. Seven water samples at different residence times in the PVC pipe were taken for analysis. Results are summarized in Table 34. A comparison of the data from the two sets of samples indicates that concentration of both MEK and THF in the second set were reduced to 1/2 of the concentration in the first set. About 2,400 gallons of water were used during the period of samples taken between Set I and Set II. This water presumably removed some of the MEK and THF from PVC pipe cement in the pipe.

TABLE 34. CONCENTRATION (PPM) OF MEK AND THF IN WATER SAMPLES AT VARIOUS RESIDENCE TIMES IN THE PVC PIPE (110)

Residence Time (h)	Samples Taken 6 Months After Pipe Installation		Samples Taken 8 Months After Pipe Installation	
	MEK	THF	MEK	THF
0	0	0	0	0
4	0.4	1.0	0.1	0.7
8	0.6	1.7	-	-
16	1.8	5.8	0.6	2.4
24	2.2	8.9	1.1	3.7
48	3.9	12	2.1	6.8
64	4.5	13	-	-
72	-	-	2.2	7.5
96	4.5	13	-	-

Another series of tests, however, found that concentrations of MEK, THF, cyclohexanone, and dimethylformamide (DMF) did not attain hazardous levels in static water or usage simulation tests (103). An analysis based on results of the tests stated that levels of the four solvents declined to less than three parts per million in less than three weeks of static exposure and that no significance in solvent leaching appears between poorly constructed solvents cement joints and well constructed solvent cement joints. Testing was performed by a private consulting engineering firm while the analysis presented was performed by representatives of the plastic resins, pipe, fittings, and solvent manufacturers. Research in this area is currently proceeding and should help to clarify the reported discrepencies concerning release extents and possible health concerns from organic solvent leaching.

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SECTION 5

CORROSION MONITORING AND DETECTION

Detection of degradation and measurement of corrosion will be desirable for assessing the corrosivity of a given water, determining the efficacy of water treatment or inhibitor programs, and evaluating health effects of water system corrosion. The procedures involved in corrosion testing are deceptively simple in the sense that measurements can be obtained using relatively simple procedures. The detailed preparation of specimens and apparatus, however, is critical to obtaining reliable numbers. And the design of the experiment and use of the results for prediction requires consideration of many aspects of corrosion. This section describes the basic test methods applicable to corrosion in potable waters and gives references to more detailed procedures.

The following general methods are discussed in this section.

- specimen exposure for an extended duration followed by examination and weight-loss determination,
- electrochemical measurement of "instantaneous" corrosion rates, and
- chemical analysis for changes in concentration of a chemical species resulting from corrosion.

As with all corrosion tests, the value and reliability of these methods will depend on proper planning and execution of the details involved in the procedures. The applicability of a given procedure will depend on the objectives of the tests.

This discussion is intended to apply primarily to testing under field conditions (in the water treatment plant or distribution system). Testing under laboratory conditions requires careful preparation and control of the corrosive environment in addition to the other precautions. As in the rest of this report, external corrosion will not be considered.

SPECIMEN EXPOSURE TESTING

Placement of a test specimen in the corrosive environment and examination after some exposure duration is the oldest corrosion test method. While fundamentally simple, there are a number of details which must be considered. One of the most basic considerations is that the test specimen should "see" the same environment as the equipment of interest. This environment includes the chemical content of the fluid, the temperature, flow rate, galvanic coupling, periodic environment fluctuations, entrained solids or gases, etc. While the test specimens cannot be exposed to exactly the same environment as a given material in a water supply system, placement should be chosen to be representative of the application of that material. It is often necessary to consider the effect of specimen placement on the properties of the environment such as flow patterns and chemical content. Because corrosion is a function of electrochemical kinetics and surface phenomena, it is not surprising that surface preparation of specimen and careful documentation of metallurgical history are important procedural considerations. Planning and evaluation of tests should be done after careful review of factors affecting the known corrosion behavior of the materials in similar environments.

The general procedures used for corrosion testing can be delineated as follows:

- Selection of materials and specimens. Care should be taken that factors such as heat treatment and chemical composition are known and representative of the actual pipe or equipment of interest.

- Surface preparation. Actual equipment surfaces generally cannot be duplicated, but efforts to approach them with a reproducible preparation method must be made.

- Measuring and weighing. Both surface area and weight must be accurately measured with care taken to avoid fouling the surface.

- Exposure technique. Proper placement should be maintainable for the entire test period.

- Duration. Exposure time and an examination program should be carefully planned before starting the test period.

- Examination and cleaning of specimens after test. This step is important where documentation and use of proper technique is critical.

- Interpretation of results.

Details of these steps are discussed in large part by Fontana and Greene (4). Procedures are also given in standards or recommended practices by the American Society for Testing and Materials (ASTM) and the National Association of Corrosion Engineers (NACE). The main ASTM publication is the Standard Recommended Practice designated G4 on Conducting Plant Corrosion Tests which gives general guidelines and information on apparatus, test specimen preparation and placement, test duration, specimen removal and examination, and reporting (2). The ASTM Standard Recommended Practice G1 gives additional details on preparing, cleaning, and evaluating corrosion test specimens (1). Another useful guide is the NACE Standard TM-01-69 (1976 Revision) on Laboratory Corrosion Testing of Metals for the Process Industries (12). Use of this guide in potable water corrosion control testing has been described by Mullen and Ritter (11).

The size and shape of test specimens depends on several factors and cannot be rigidly set. It is generally desireable to have a high ratio of surface area to mass to obtain maximum corrosion loss. While the sample should be as large as possible, it should not exceed the weight limitations of the usual analytical balances (about 160 grams) or present problems in placement in pipes or equipment. Thin sections can be used to satisfy several of these requirements but the specimen should not be so thin as to be perforated by corrosion or to lack reasonable mechanical stability. The edges of specimens should be finished by polishing or machining to eliminate cold-worked metal. Specimens with sheared edges should not be used. Any dirt or heat-treated scale should be removed and the specimens should be freed from water breaks by suitable cleaning. Metal specimens should be abraded to at least 120 grit surface finish. The specimen should be stamped for identification, weighed to the nearest 0.1 mg on an analytical balance, and their surface area accurately determined.

A number of methods can be used for supporting specimens for exposure. The main considerations are that the corrosive media should have easy access to the specimens, the supports should not fail during the tests, the specimens should be insulated or electrically isolated unless the study of galvanic effects is intended, and the desired degree of immersion should be obtainable. Ready access to the specimens is also desireable. Apparatus for mounting specimens is described in detail and with mechanical drawings in ASTM G4-68 (2). They describe a spool rack in which specimens with a hole drilled through their center are positioned on a metal support rod which is covered with insulating plastic. Plastic tubing spacers also spooled on the center rod keep the specimens separate and supported. Insulating end disks are provided and the assembly is completed by nuts which are tightened on either end of the support rod. Other support methods are based on similar principles. They should be tailored to fit the equipment and operating conditions at hand.

Misleading results may be obtained if exposure duration and number of exposure periods are not carefully selected. It is often found that initial corrosion rates are considerably higher than those obtained after some time. However, in some cases pitting or crevice corrosion may not occur until after a certain incubation period. In general, tests run for long periods are considerably more realistic than short term tests. For uniform corrosion, a very rough guide for minimum exposure time suggested by both ASTM and NACE is given by:

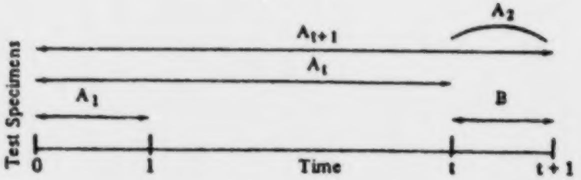
$$\text{duration of test (hour)} = \frac{2000}{\text{corrosion rate (mpy)}}$$

This guideline is based on the general rule that the lower the corrosion rate, the longer the test should be run. The guide can be used with an estimated lower limit of corrosion rate or used to decide if tests should be repeated for a longer period based on existing results.

Most sources recommend using the planned-interval test originally proposed by Wachter and Treseder for setting up tests and evaluating results. This procedure allows evaluation of the effect of time on corrosion of the specimen and also on the corrosiveness of the environment. The procedure and evaluation of results are given in Table 35 along with an example of its application. This procedure is recommended by NACE TM-01-69 and also by Fontana and Greene (4).

After removal from the test environment the appearance of the test specimens and the rack should be noted. Specimens should be washed in water to remove soluble materials from the surface. Color photographs of the specimens should be made. The appearance and degree of adhesion of any coatings or films or the surface should be noted. If possible, samples of the corrosion product films should be preserved for future study. Specimens are not generally weighed until corrosion products are totally removed, since metal converted to corrosion product is structurally lost. But for potable water studies, additional information on the addition of species to the water stream might be obtained by also weighing the dried specimens at this point. Following this, the corrosion layers should be removed by a method that does not affect the base metal. The cleaning procedure is critical and will depend on the base material as well as the nature of the corrosion products. Procedures may include light mechanical cleaning (eg. rubbing with a rubber stopper), electrolytic cleaning, and chemical cleaning. Detailed procedures are given in ASTM G1-72 and in Fontana and Greene (1, 4). The possibilty of solid metal removal should be checked by applying the proposed method to fresh and to already cleaned, dried, and weighed specimens to determine any additional weight loss. After cleaning, the specimens should be dried and weighed to the same accuracy as the initial pre-test weighing. Weight-loss corrosion rates should be calculated for uniform corrosion cases. The specimens should be carefully examined visually and any modes of degradation such as pitting, crevice corrosion, dealloying, or other attacks noted. Photographs of the specimens should again be made since cleaning will often disclose more features of attack. If pitting occurs the maximum and average pit depths should be measured and also the number, size, general distribution, and shape of the pits should be noted. Distinction should be made between pits which occur under insulating spacers and those on exposed surfaces. The former is probably related to crevice corrosion. The depth

TABLE 35. PLANNED INTERVAL TEST (4)



Identical specimens-all placed in the same corrosive fluid. Imposed conditions of the test kept constant for entire time t + 1. Letters, A_1, A_t, A_{t+1}, B, represent corrosion damage experienced by each test specimen. A_2 is calculated by subtracting A_t from A_{t+1}.

Occurrences During Corrosion Test		Criteria
Liquid corrosiveness	unchanged	$A_1 = B$
	decreased	$B < A_1$
	increased	$A_1 < B$
Metal corrodibility	unchanged	$A_2 = B$
	decreased	$A_2 < B$
	increased	$B < A_2$

Combinations of Situations

Liquid Corrosiveness	Metal Corrodibility	Criteria
1. unchanged	unchanged	$A_1 = A_2 = B$
2. unchanged	decreased	$A_2 < A_1 = B$
3. unchanged	increased	$A_1 = B < A_2$
4. decreased	unchanged	$A_2 = B < A_1$
5. decreased	decreased	$A_2 < B < A_1$
6. decreased	increased	$A_1 > B < A_2$
7. increased	unchanged	$A_1 < A_2 = B$
8. increased	decreased	$A_1 < B > A_2$
9. increased	increased	$A_1 < B < A_2$

Example of Planned Interval Corrosion Test

Conditions: Duplicate strips of low-carbon steel, each 3/4 by 3 inches (20 x 75 mm) immersed in 200 ml of 10% $AlCl_3$ - 90% $SbCl_3$ mixture through which dried HCl gas was slowly bubbled at atm. pressure. Temperature 90 C.

	Interval, days	Wt. Loss, mg	Penetration, mils	Apparent Corrosion Rate, mils/yr	mmpy
A_1 . .	0-1	1080	1.69	620	15.7
A_t . .	0-3	1430	2.24	270	6.9
A_{t+1} .	0-4	1460	2.29	210	5.3
B . . .	3-4	70	0.11	40	1.0
A_2 . .	calc. 3-4	30	0.05	18	0.5

$A_2 < B < A_1$
$0.05 < 0.11 < 1.69$

Therefore, liquid markedly decreased in corrosiveness during test, and formation of partially protective scale on the steel was indicated.

of any crevice corrosion should be determined. Pitting rates are often ambiguous and no extrapolations should be made. The actual pit depth and length of exposure should be reported. Selective or localized attack can be examined and recorded in greater detail by metallographic and microscopic techniques.

Metals which may be susceptible to dealloying or stress cracking should be bent after other examination and the development of any cracks should be noted. These results should be compared to similar bend tests with unexposed specimens (2).

ELECTROCHEMICAL TEST METHODS

Electrochemical methods for corrosion measurement are more complicated than specimen exposure testing with respect to both equipment and interpretation. Electrochemical methods are also relatively new and less established than the conventional exposure tests. When properly applied, however, the newer methods offer several advantages. The electrochemical methods of main interest are very rapid and can be used for near-continuous monitoring of corrosion rates under proper conditions. They are adaptable to measurement of low corrosion rates which are most difficult to measure by weight loss. Because the most often used electrochemical methods do not significantly affect the specimen, time profiles of corrosion rates can be obtained. Also, the effects of various water treatment methods can be monitored on a given specimen.

The electrochemical measurements will be most reliable when the metal of interest undergoes uniform corrosion in systems where scale formation is minimal. The care required for sample preparation and placement is as important for these methods as for the simple specimen exposure methods discussed above. One important limitation on the use of electrochemical methods to obtain rapid corrosion measurements is that the corroding behavior of a metal often depends on the length of time it has been exposed to a given environment. Electrochemical methods can provide "instantaneous" corrosion rates, but variation of corrosion rates with time must also be considered.

The basis of these methods is the electrochemical nature of the corrosion of metals in aqueous solutions. The methods are not applicable to nonmetallic materials used in water supply systems. The rate of electrochemical reactions, and thus the rate of corrosion reactions, can be expressed as an electrical current. The driving force for obtaining the reaction giving rise to the current is an electrical potential difference. In the general case, the relation between current and potential difference for electrochemical reactions is non-ohmic (i.e., nonlinear); generally an exponential or complex mixed relationship is seen. However, for small deviations in driving force from some steady state, or open circuit corrosion potential, the current and potential difference are approximately ohmic or linear. Use of such small potential deviations (i.e., small polarization) methods forms the basis for practically all commercial electrochemical corrosion rate instruments and methods proposed for field or routine use. They are often referred to as "linear polarization" or "polarization resistance" methods. It is noteworthy that the use of these small perturbation methods also causes less change in the specimen surface and makes possible multiple measurements with the same specimen. Even small perturbations are of some concern. However, tests of repeatedly polarized cast iron specimens in a potable water environment gave generally the same results as freely corroding samples (10). The possibility of differences occurring with other metals should be considered.

The derivation of current-potential relationships for linear polarization conditions has been described for various degrees of model sophistication (4). A widely used form is given by the equation:

$$\frac{\Delta E}{\Delta i} = \frac{\beta_a \ \beta_c}{(\log 10) i_{corr} (\beta_a + \beta_c)}$$

In this equation, ΔE is the deviation from the corrosion potential, Δi is the current density (current per unit area of electrode specimen), i_{corr} is the corrosion current density which can be related to the corrosion rate, and $\beta\alpha$ and βc are parameters (so-called Tafel slopes) associated with the electrochemical kinetics of the individual anodic and cathodic corrosion reactions. At least to a first approximation, $\beta\alpha$ and βc are constants for a given corrosion system. For model systems, β values are such that the following simple form is obtained.

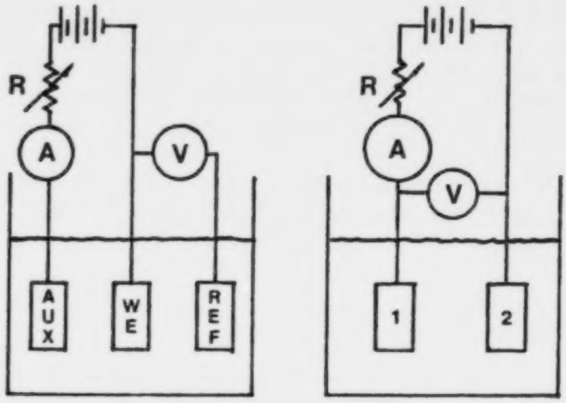
$$\frac{\Delta E}{\Delta i} = \frac{RT}{F} \cdot \frac{1}{i_{corr}}$$

where RT/F consists of fundamental constants and the absolute temperature. The value of RT/F is about 0.026 volts at 25°C. These equations are applicable for ΔE values of 20 millivolts at most, and smaller ΔE values are probably preferable. The simple form often gives useful approximations; although absolute errors may be large in case of unequal Tafel slopes, relative measurements may still be useful. The quantity i_{corr} (microamperes) can be related to the corrosion rate by the following equation:

$$\text{Corrosion Rate (mpy)} = \frac{0.129 \ i_{corr} \ A}{nD}$$

Here A is the atomic weight of the metal, n is the number of electrons lost by the metal atom during corrosion (eg. $n = 2$ for iron going to Fe^{+2}), and D is the metal density (g/cm^3). In some commerical instruments the conversion factors are set by specimen size and electronic means to give direct readouts of corrosion rates.

There are a number of means of actually carrying out the linear polarization measurement. There does not appear to be a definitive study to determine if any particular method is superior for use in potable water type systems. Schematics of two types of electrode circuits are shown in Figure 34. The three-electrode method is widely used and employs a test specimen electrode,



3-Electrode 2-Electrode

Figure 34. Schematic of 3 and 2 electrode circuitry.

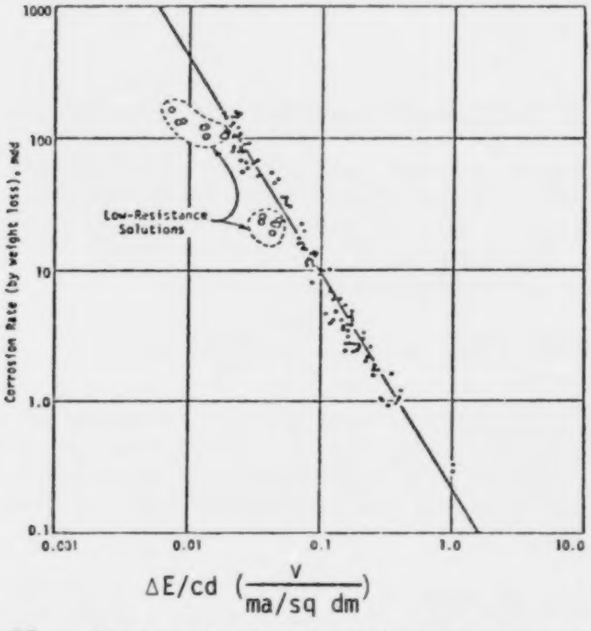


Figure 35. Empirical relationship between initial slope of polarization curve (resistance) and corrosion rate determined by weight loss. (7)

an auxiliary electrode and a reference electrode. External current flows only through the test and auxiliary electrodes while the polarization of the test electrode is measured by way of the referenced electrode. The degree of polarization may be set at some constant value, 10 millivolts is often used,or varied in the vicinity of the corrosion potential. It is also possible to use two identical electrodes for test and auxiliary and measure potential difference between these two along with the current, without using a reference electrode. Comparison of three-electrode and two-electrode methods have been given, along with a general analysis of errors in linear polarization methods, by Bandy and Jones (3). This method is intended to measure only the equivalent resistance of the corrosion reaction rate and, therefore, care should be taken that other resistances such as that of the solution or connectors are small and that abnormal scale or fouling of the test electrode does not occur.

The applicability of the linear polarization method to certain potable water systems was first demonstrated by Larson (7). The close correlation found between corrosion rates obtained by weight loss measurement and the linear polarization resistance is shown in Figure 35. These results were obtained for cast iron and steel in potable water environments of various composition. Several other evaluations of the linear polarization method in potable waters have been reported (10,9).

Polarization curves can be recorded by the potentiodynamic method in which the potential of the test specimen is electronically varied at a preset linear rate and recorded along with the resulting current. For general use the potential excursions can be limited to about ± 10 millivolts of the open circuit voltage to decrease the chance of modifying the surface by polarization. The potential scan rate should be low enough that current due to double layer charging is negligible compared to the faradaic current. The method has the advantages of providing a better measure of the current-voltage slope which is the desired measurement and a readout by which any departure from linearity of this plot can be obtained. This is obtained at the cost of increased complexity in instrumentation and operation.

The linear polarization method has promise for rapid estimates of the corrosivity of potable waters. It must be applied with care and time must be taken to ensure that metal specimens have reached a steady-state corrosion rate. With careful use, it should be possible to monitor the relative effects of various treatment methods using these procedures. A number of probes of the same material should be used and periodic inspection for localized corrosion or scaling should be done. Integration of the instantaneous rates and comparison with weight-loss specimens should be done for confidence in absolute rates derived from linear polarization methods.

Linear polarization methods are applicable to uniform corrosion or at best averaging small areas of pits with large uniform areas. Electrochemical methods for determining localized corrosion susceptibility are being evaluated under laboratory conditions, but have not been standardized. Potential applications of such methods to field testing has recently been discussed by Martin (8). Additional work is needed to develop these methods for use in potable water environments.

Another electrical, but not electrochemical, method for determining corrosion rates is based on measuring the change in electronic resistance of a metal specimen. As the relatively thin wire, tube or strip specimen element corrodes, its electrical resistance increases due to the decrease in cross sectional area. Measurements of resistance over a period of time (several days or weeks) give an estimate of the change in specimen thickness and, thus, a corrosion rate can be obtained. Results can be obtained more quickly than with coupon tests, but are not "real time" in the sense of linear polarization tests. For uniform corrosion behavior, the method is relatively direct.

Reedy has described the field use of this type of resistance probe for testing a number of metals in two natural water sources (13). A stabilization period of 10-14 days immersion was required before consistent corrosion rates were obtained. This result was probably due to the normal surface changes that occur on exposure of a fresh metal specimen to a corrosive environment. Long-term testing (50 days) confirmed that reproducible results could be obtained after the initial period.

CHEMICAL ANALYSES FOR CORROSION PRODUCTS

Corrosion can be inferred from the increase in concentration of a metal species in solution from one point in a water distribution system to another point downstream of the first. Although this analysis is not a conventional means of corrosion measurement, it provides a direct measure of the quantity of interest and, in many cases, may be the only way of determining a health hazard if construction materials are unknown or access to the distribution system is difficult. Due to the uncertainties involved, this procedure will probably serve best as an indicator of potential corrosivity of a water system and the need for application of more quantitative corrosion rate methods.

Sampling points and procedures will be dictated by the information desired. To obtain baseline samples without any contamination by piping, raw water samples should be dipped from surface sources, or for groundwater supplies collected as close to the well as possible. In all cases samples for trace metal analysis should be preserved with ultrapure nitric acid in thoroughly cleaned sample bottles. Finished water samples can be obtained after treatment at the treatment plant. Sampling in homes can be set up to provide some differentiation between sources of metal contamination. Karalekas and coworkers describe the following sampling program (5, 6). The water samples were collected at the kitchen sink the first thing in the morning before any water was used in the house.

- Interior plumbing sample; this is collected immediately upon opening the faucet and represents water that has been standing overnight in the fixture and plumbing serving the faucet,

- Service line sample; this is obtained after the sample collector feels the water temperature change from warm to cool, representing the water in the service line to the house,

- Water main sample; this is collected after allowing the water to run for several minutes and represents water from the main which has had minimum contact time with the service line and interior plumbing.

These samples provide a representation of the range of trace metal concentrations the consumer is likely to experience as well as an indication of the source of the contaminant.

Although the comparison of chemical analyses from several points seems to provide a simple procedure, there are several complications. Because a difference of two experimental numbers is required, the analytical methods must be both accurate and precise. Surface water supplies may have trace metal contents from a geochemical origin. Trace materials may also be introduced by airborne or waterborne pollutants or as impurities in chemicals added to the water during the treatment process. In analyzing any trace component in water, care must be taken during sampling, sample storage, and sample pretreatment to avoid large systematic errors due to such problems as contamination by equipment, precipitation or adsorption of the measured species, or contamination by impurities in reagents used for sample preservation or pretreatment. The dependence of material concentration on system flow history is well documented with regard to "stagnant" versus "free-flowing". More complicated behavior may also occur in distribution or household systems as corrosion products precipitate or undergo redox chemistry or adsorption. Corrosion products may spall from walls or be released from pits at irregular intervals. The sorption of relatively large quantities of lead and copper ion by hydrous ferric oxide has been studied (14). Materials such as hydrous ferrous oxide could exist either as a layer attached to iron pipes or in suspension. In view of these considerations, reliable results may often require taking a large number of specimens or continuous monitoring over a period of time.

If the materials in use in the water system are unknown or are not well defined, the chemical analysis method for corrosion products is further complicated. Some chemical analyses are expensive, and performing tests for large number of possible contaminants may be cost prohibitive for small public or private water systems. Additionally, specific corrosion products can result or appear from the use of various materials.

Analytical procedures used to quantify the existence of asbestos minerals in water are severely limited and are subject to produce erroneous results. Primary reasons for the extreme difficulty in determining asbestos fiber concentrations in water include 1) asbestos fiber concentration in potable water is generally very low, 2) chemical analytical methods are not applicable because elements present are common to all rock-forming minerals, 3) asbestos fibers cannot be concentrated or separated from other inorganic solids present in the water, and 4) fiber sizes are often below the resolution of the optical microscope (15). Also, a knowledge of field operations is necessary to determine the possibility of fiber release resulting from drilling and tapping as opposed to regular deterioration.

One technique employed to analyze asbestos fiber concentrations or counts in water utilizes the electron microscope. Using this technique, solids are removed from the water sample by filtration on a membrance filter and the entire sample is ashed to destroy the filter and any organic and oxidizable inorganic solids that may be present. The inorganic residue is then rubbed out in a dilute solution of nitrocellulose to reduce the particle sizes and transferred to a standard electron-microscope grid. This sample is examined under an electron microscope and the presence of chrysotile fibers is quantified by measuring the length and diameter of each fiber, calculating the total mass and finally relating this mass to the original amount of water sampled. This technique is specific to chrysotile fibers because of their recognizable hollow-tube structure.

The accuracy and precision of this anlysis is very poor because only an extremely small fraction of the sample can be examined and this sample generally contains only a small amount of asbestos. Analysis of samples using the electron microscope technique cannot be duplicated by better than a factor of three, and it is estimated that the measured value is accurate to within a factor of ten of the true value. Therefore, measured values should be considered indicators or indices of the relative amount of fiber present. Another limitation of this technique is that the analysis is specific to the structurally recognizable chrysotile fibers. Several other varieties of asbestos materials may be present in water such as crocidolite which is also a component of most asbestos-cement pipe (15).

Development of analytical methods for trace material determination has coincided with growing environmental concerns. A critical evaluation of the many developing methods is outside the scope of this report. Three of the more popular methods for the metals likely to be of interest are atomic absorption spectroscopy (AAS), anodic stripping voltammetry (ASV), and neutron activation analysis (NAA). Use of NAA requires access to a reactor. AAS often requires considerable sample pretreatment as well as equipment usually restricted to a permanent laboratory. Continuous monitoring of tap water for Pb, Cd, and Cu has been demonstrated using ASV and related techniques by National Sanitation Foundation personnel (9). The number of elements that can be analyzed by this method is relatively small, but they correspond well to those of interest from a corrosion and health standpoint. The instrumentation required for ASV is somewhat complicated, but portable.

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SECTION 6

CORROSION PREVENTION AND CONTROL

Corrosion control in potable water systems is most commonly attempted by establishing a protective barrier between a corrodible material surface and a corrosive water. This protective barrier can be applied mechanically as a material coating or lining prior to installation of facilities or it can be applied chemically by adjusting the water quality characteristics of the potable water to precipitate a byproduct which forms on the surface of water system materials. The most commonly used pipe coatings include coal tar enamels, epoxy paint, and cement mortar. Water tank linings generally include coal tar enamels and paints, vinyl, and epoxy. Other coatings and linings which are also used are hot and cold applied petroleum based waxes, zinc paints, and asphalt. Any applied coating or lining must be environmentally sound, including their application procedures, and must not impart objectionable aesthetic or health effects into the water.

The addition of lime to induce calcium carbonate precipitation and form a protective coating chemically is the most commonly used and accepted method of corrosion control through water quality adjustment. Chemically applied protective coatings are also formed by the addition of sodium silicate and inorganic phosphates. These chemicals are generally referred to as corrosion inhibitors.

Other corrosion control practices include adjusting the water quality characteristics to render potable waters less aggressive or less corrosive. As previously discussed, corrosive waters are generally characterized as containing high dissolved oxygen and/or carbon dioxide, low alkalinity and hardness, and low pH. Adjusting these parameters for optimum corrosion control of a specific material is sometimes practiced or attempted, but optimum conditions are often difficult to determine.

Corrosion control alternatives currently being practiced and available to the water works industry are discussed in this section. Also included in this section is a brief description of the case history of the Seattle Water Department attempts to correct or retard corrosion in its potable water supply facilities. Their attempts emphasize the magnitude of the problems and difficulties in implementing a corrosion control program. A list of the applicability of the mechanically applied linings and corrosion inhibitors discussed is presented in Table 48 (Section 7):

MECHANICALLY APPLIED PIPE LINING AND COATINGS

As early as 1860, attempts to solve corrosion problems in water pipes resulted in dipping cast iron pipe in a bituminous coating material, and cement lining was suggested by the French Academy of Sciences. By 1930, the use of a cement mortar lining for pipes used in water distribution systems was specified in eastern and southeastern areas of the United States, while many areas in the Midwest specified coal tar coatings. Professional papers in the 1930's and 40's (13, 14,21) extolled the virtures of cement lined iron and cast iron pipes for removing "red water" problems, but inconsistencies between different systems prompted comparison investigations in the 50's (3,50). These papers reported tubercule formation and corrosion resistency for various cement, bituminous dips and enamels, pitch, tar dip, and asphalt sealed cement linings on iron pipes. Water tank corrosion was controlled with paint coatings or cathodic protection which were gradually replaced with coal tar enamel. More recent technologies have produced vinyl, epoxy, chlorinated rubber, and other tank linings. The focus of current research is to determine the extent of trace organics released and subsequent public health affects from the use of bituminous based linings.

The three principal pipe linings currently used for corrosion protection are coal enamel, epoxy, and cement mortar.

Hot Applied Coal Tar Enamel

Hot applied coal tar enamel is produced from coal tar pitch, a residue in the fractional distillation of coal tar obtained from the destructive distillation of bituminous coal. Coal tar used in potable water systems is required to meet AWWA specifications for type of coal and production process. Coal tar enamel is made by dispersing coal in a mixture of coal tar pitch and coal tar gas oil. Talc is added to provide strength.

Hot applied coal tar enamel is used in steel pipes, and it is estimated that between 50 and 80 percent of all steel pipe used for water distribution is lined this way. The coating process involves spraying a primer coat, usually a chlorinated rubber based resin, on the cleaned surface. After the primer dries, the coal tar enamel is heated to a fluid consistency and poured on the pipe surface from a trough extending lengthwise through the rotating pipe. Fittings are manually lined. Thickness of the coating is 0.094 inches (2.4mm). If connections are to be welded, field touch-up around welded joints is necessary.

Hot applied coal tar enamel was used to line steel water pipelines in New York City as early as 1914. Coal tar enameled pipes, inspected after many years of service in water supply systems, have shown no coating failures when the lining was properly applied. Service life of this lining is relatively long, often in excess of 50 years. Other advantages include good erosion resistance to silt or small amounts of sand in the water and resistance to biological attachments. Disadvantages include the need to re-apply to welded areas and to use special care in handling pipes during weather extremes as cold causes brittleness and heat may initiate cracking. An increase of trace organic compounds exists in water flowing through coal tar lined pipe, but the potential effects of their release is presently unknown. The extent of this release is currently under investigation at the EPA laboratory in Cincinnati, Ohio.

Epoxy

Epoxy paint coatings have been used to line steel water pipes since the mid 1960's and are becoming increasingly popular. Two types of epoxy systems exist: single component and double component. The former consists of an epoxy resin, pigments, drying oil, and a reactive resin. Drying results from oxidation and polymerization. The latter consists of a base containing the epoxy resin, pigment, and solvent and a polyamide or amine and solvent hardener.

The lining is usually applied in the field because welding will burn off the epoxy and re-application can be avoided. The pipe is first cleaned and a phosphate treatment or rust inhibiting zinc silicate primer is applied to the surface. This step is not necessary, but it improves the epoxy adhesion and abrasive resistance. Two coats of epoxy are then applied by spraying from a "pig" pulled through the pipe.

A major advantage to using epoxy linings is the high smoothness coefficients (Hazen-Williams coefficients of 138-172 (17)) produced and the corresponding reduced pumping costs. Also, epoxy paints can be formulated from components approved by FDA for food contact surfaces. Principal disadvantages include cost and a reduced resistance to abrasion, compared to coal tar enamel, which limits service life to under 15 years.

Recent use of powdered epoxy coatings have reduced occupational health and air pollution problems associated with solvents necessary for spray applications. The powder is sprayed onto the heated surface and melts to a thin film that fuses to the pipe. Because epoxy linings have been used to line steel water pipes for fewer years than their anticipated service life, case histories are currently just being developed. In 1964, however, the installation of 20,000 feet of epoxy lined 30-inch force main by an eastern Pennsylvania water company resulted in lower construction costs and a more beneficial Hazen-Williams coefficient. As a result, the company installed an additional 28,000 feet of epoxy lined 20- and 30-inch lines and, 10 years after the 1964 installation, was planning further installations (17). It is also reported that three pipeline companies use only epoxy to line their steel pipes (19).

Cement Mortar

Although being used less to line steel pipes, cement mortar is the only coating used to line cast iron and ductile iron pipes. Cement linings are applied by introducing a slurry into a rotating pipe. Centrifugal action distributes the mix to a uniform coating. An alternative process involves using a rod with a revolving head. The rod is pushed through the pipe, and the slurry is sprayed onto the surface of the pipe. Composition of the applied slurry depends on the size of pipe being lined. Pipes under 20 centimeters in diameter use a cement : sand : water weight ratio of 2 : 3 : 1, whereas larger pipes use a ratio of 2 : 4 : 1 to control possible cracking.

Proper curing of the lined pipe is important. Steel pipes are cured by sealing the ends, spraying water on the lining, or alternating applications of steam and water. Mortar in cast iron and ductile iron pipes is coated with a thin (0.001 inch, 0.0254mm) layer of an asphalt, mineral spirit, and xylene sealant. This process provides a moisture barrier, constraining water in the slurry, promoting a proper slow cure. This sealant has the added advantage of preventing decalcification of the lining in soft waters.

Advantages to using cement mortar lining include its cost and low sensitivity to variations in the substrate quality or application procedures. It can be applied in situ on pipes whose lining has failed provided the loosely coated areas are removed. Because the corrosion abatement mechanism is a result of the calcium hydroxide released in addition to the physical barrier, uncoated metal at pipe joints is protected. Also, surface fissures will heal themselves when immersed in water.

The rigidity of the lining is a disadvantage because pipes subject to deflections may experience lining cracking and sloughing. Also, the depth of the coating reduces the cross sectional area of the pipe, and hence its carrying capacity significantly. For example, the area of a 20-inch I.D. pipe with a cement mortar lining is reduced 6 percent. A coal tar enamel lining reduces the area 2 percent, and an epoxy lining reduces the area by less than 0.2 percent. Also, decalcification in soft, calcium dissolving waters may impart an objectionable taste to the water.

The first applications of cement mortar linings for steel water pipes was in the late 1800's and some of these pipes have been in use since that time. Cement lined sheet-iron pipes were also common at that time and, if designed and installed properly, provided a 40 to 50 year service life. The first cement lined cast iron pipe was installed in America in 1922, so the articles published in the 1930's and 1940's citing the longevity of cement lined pipes were in reference to the steel lined pipes. Published literature of the 1950's (2, 46) indicated the widespread use and acceptance of cement lined cast iron pipe, but academic decisions were being deferred pending further use. Today, cement mortar is the only lining used in cast iron and ductile iron pipe.

TANK LININGS AND COATINGS

The principal types of water tank linings are coal tar enamels and paints, vinyl, and epoxy. Other coatings exist and are mentioned, but they are either no longer or not extensively used. Water tank linings should exhibit ease of application, effective corrosion control, and good erosion resistance.

Coal Tar Based Coatings

Hot applied coal tar enamel is prepared and used as discussed in the pipe lining section. This coating has a tendency to sag or ripple when applied above the waterline when the tank walls are heated. Hot applied coal tar enamel is the primary coal tar based coating used to line water tanks.

Coal tar paints are often used to reline existing water tanks. Cold applied coal tar paint is prepared by adding coal tar solvents such as xylene or naptha to coal tar enamel. It is brushed or sprayed on the surface to form a relatively thick film resistant to sags or runs. Because it can impart unpleasant tastes and odors to the water, its use is restricted to above waterline surfaces. It is less durable than hot applied coal tar enamel and has a service life of 5 to 10 years. A tasteless and odorless cold applied coal tar paint is produced by combining coal tar enamel with solvents free of phenols and other taste and odor constituents. This paint may be used below water, but should not be exposed to sunlight or ice.

Coal tar epoxy paints used to line potable water tanks are generally two component systems. One part consists of a coal tar pitch base with a polyamide resin, magnesium silicate, xylene, ethyl alcohol, a gelling agent, and a catalyst added. The second part is a liquid epoxy resin. Some types of coal tar epoxy paints sold do not conform to the Steel Structure Painting Council specifications and may produce taste and odor problems in the water. Coal tar epoxy paints are less resistant to abrasion than coal tar enamel. Exposure to sunlight causes chalking to occur, but if this exposure is eliminated, coal tar epoxy paints may provide a service life of over 20 years.

Coal tar urethane paints have been inconsistent in their service lives. Some applications have provided a 25 year service life, but other applications have failed within one year. This type of lining is not presently marketed.

Coal tar emulsion paint is a water based suspension of coal tar pitch, magnesium silicate or other mineral filler, and a rust inhibitor. Although it has good adhesive characteristics, is practically odorless, and resists sunlight degradation, it is not as watertight as organic solvent coal tar coatings. Consequently, its use below the waterline is limited.

Investigations have shown that trace organics are released into water stored in coal tar base lined tanks. The results of analytical tests on water stored in a coal tar lined tank are shown in Table 36a. Possible health affects associated with these organics in the concentrations observed are not presently known. Research presently being done on the release of these organics, including rates, solubilities in water, and identification of decomposition products will have to be combined with toxicological evaluations to determine future uses or restrictions on coal tar based linings.

Vinyl

Vinyl paints are a mixture of a vinyl chloride-vinyl acetate copolymer with a hydroxyl compound and/or a carboxy compound. These paints are applied on steel in either a three-coat or a four-coat system, with different formulations used in each system and within the five-coat system. Vinyl paints are inert in water and produce a hard, smooth surface. Soft water conditions may reduce the expected service life of 20 years. Recent vinyl failures in California have been blamed on formula changes made to meet that state's air pollution criteria. Another report stated that vinyl paints do not wear well in soft waters, but one engineering consultant estimated (1977) that vinyl paints are specified for 90 percent of their storage tank projects. Although vinyls are one of the more popular water tank liners, their intricacies of application prohibit their use in pipes.

Epoxy

Epoxy is produced and applied as previously discussed in The Pipe Lining And Coating section. Like vinyl, epoxy produces a hard, smooth surface that exhibits low water permeability and strong adhesion to steel when properly formulated and applied. Reformulation necessary to conform to the California air pollution control regulations has adversely affected their performance. While most reports on epoxy linings are for pipe applications, where flow resistance co-effecients are important concerns, tests by Bethlehem Steel have indicated that epoxy wears as well as hot applied coal tar enamel in water immersion, non-abrasive, testing (17).

Other Mechanically Applied Tank Linings

Hot and cold applied wax coatings are also used to line water tanks. These coatings are blends of petroleum waxes and oil based corrosion inhibitors. These coatings may be applied directly over old rust or paint, but commercial blast cleaning of the surface prior to application is preferred. Application either by stiff bristled brushes or spray equipment is followed by torch flaming used to smooth and thoroughly close the surface. The major disadvantage to using wax coatings is a relatively short service life of approximately five years.

TABLE 36a

ESTIMATED CONCENTRATIONS OF COMPOUNDS DETECTED IN THE WATER IN THE BAYOU CASSOTTE GROUND STORAGE WATER TANK USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY (19)

Compound	Sample Date and Concentration (μg/l)				
	9/6/77		1/16/78	2/21/78	
	A	B	A	A	B
naphthalene	5.4	6.7		1.3	2.7
methyl naphthalene	0.75	1.4	0.63	<1	1.3
biphenyl	0.21	0.40		<1	<1
acenaphthene	2.8	4.6	1.3	3.1	8.0
dibenzofuran	3.1	5.0	1.1	2.3	6.3
fluorene	3.4	5.1	1.5	2.9	8.0
phenanthrene/anthracene	8.7	9.3	4.5	14	35
carbazole	0.70	1.3	0.44	3.9	11
bromoform	<10	<10	<10		
C_4 alkylchlorobenzene	<50	<50	<50	2.7	7.3
indene	<10	<10			
C_3 alkylbenzene	<10	<10			
anthraquinone	<10	<10	<10	2.3	8.3
methyl benzofuran	<10	<10		<1	1.0
quinoline	<10	<10		<1	<1
methyl styrene/indan/indene	<10	<10		1.7	2.6
methylene phenanthrene/methyl phenathrene	<10	<10	<10	1.2	4.0
pyrene	<10	<10	<10	2.2	7.0
2,5-diethyltetrahydrofuran			11		
dimethyl naphthalene				1.2	2.7
fluoranthene				2.7	9.7

A Sample obtained from a valve approximately 3 feet above the bottom of the tank

B Sample obtained from the top of the tank

Metallic sprayed zinc coating is a relatively expensive process where zinc wire is melted, atomized at a high pressure, and sprayed onto the surface. The application requires special skills and equipment, but the coating provides excellent rust inhibition and a service life of 50 years. Surface preparation by blast cleaning with one of three specified grits is mandatory.

Zinc-rich paints, containing 80-95 weight percent zinc dust, will provide a hard, abrasion and rust resisting surface on steel. The cost is high, and surface preparation involves near-white blast cleaning.

Chlorinated rubber paints may be used when the control of fumes from the application of other linings is difficult or where their use is specified as in Baltimore County. Chlorinated rubber compounds are formed by exposing natural rubber to chlorine gas. Because the resultant material is brittle, plasticizers or linseed oil are added, producing a more flexible and adherent coating. Application requires a near-white, blast cleaned surface and a zinc-rich primer. The chlorinated rubber paint is then spray applied in several coats. The intercoat adhesion is strong enough to essentially produce a single unit. This benefit provides easy surface preparation and reapplication when the orginal coating nears the end of its service life. Service lives have been estimated as 6 to 15 years.

Asphalt based linings are absorbed by water faster than coal tar based linings, and their application is generally limited to reclining existing asphalt lined tanks or sealing "green" cement mortar coating in pipes to provide a proper curing environment.

CORROSION INHIBITORS

Corrosion protection by formation of a film on the surface of a pipe may be achieved by chemical as well as mechanical means. The importance of calcium carbonate solubility in this regard was recognized in the early twentieth century by the German chemist, Tillmans, and in the U.S. by Baylis (29). Excess calcium and carbonates would form scale in pipes, reducing carrying capacities and increasing pumping requirements. $CaCO_3$ deposition in rust forming waters, however, could form an effective rust inhibitor. The need to understand the deposition-solubilization tendency of $CaCO_3$ formed the basis of the Langelier Saturation Index, a parameter formulated in 1936 but still used in corrosion control. When silicates and polyphosphates were found to inhibit corrosion, their theory and applications were investigated. Today, orthophosphates are also being studied, but corrosion control in many public water systems is still engineered from $CaCO_3$ solubility data. A summary sheet of corrosion inhibitors is presented in Table 36b.

TABLE 36b. DOSAGES AND PREFERRED WATER PARAMETERS FOR CORROSION INHIBITORS
(see text for discussion and references)

	Dosages	Velocity	pH	Alkalinity	Hardness	Additional
$CaCO_3$	Varies considerablly	Not stagnant	6.8-7.3	> 40 mg/L	> 40 mg/L	$\frac{\text{halogen + sulfate}}{\text{alkalinity}} < 0.2$ (meg basis)
Sodium Silicate	No specific concentrations usually 2-8 mg/L	Must be flowing	< 8.4 A lower pH is desired	low	very low	
Phosphates	1-2 mg/L	High velocity	< 7.0 for lead pipe	low	low	

$CaCO_3$ Precipitation

Early observations that carbonate minerals in a water supply tended to inhibit corrosion in steel and cast iron pipes led to theories on calcium carbonate deposition as an anti-corrosive mechanism as well as several indicies of corrosion that are still used in contemporary water treatment. Effective $CaCO_3$ protection depends on the presence of anodic (metal oxidation) and cathodic (oxygen reduction) reaction products in the water. Reduced oxygen, as the hydroxyl ion, reacts with bicarbonate to form water and carbonate ions. The increased concentrations of carbonate ion along with the (oxidized) metal ions (Fe, Cu, Zn, Pb) subsequently exceed the solubility product of and, consquently, form metal carbonates (1) and carbonate containing solids. If this deposit satisfactorily adheres to both itself and the pipe surface, an effective corrosion barrier forms.

Of the carbonates formed, zinc carbonate forms a less porous structure than other metal carbonates. Calcium carbonate, however, forms a solid, though soft, coating that has good adherent properties. The protective ability of a $CaCO_3$ intermeshes with existing hydrous ferric oxides and ferrous carbonate (32). Thus, the most effective use of $CaCO_3$ depends on maintaining an environment where $CaCO_3$ is slowly formed, along with corrosion products, eventually producing a hard, impenetrable coating.

Corrosion waters are generally of low pH and low alkalinity, often with high CO_2 concentrations. The introduction of a carbonate to this system will affect all three parameters because of the relationships:

$$\frac{[H^+]\,[HCO_3^-]}{[H_2CO_3]} = K_1' \qquad \text{(eq. a)}$$
First dissociation constant of carbonic acid.

$$\frac{[H^+]\,[CO_3^=]}{[HCO_3^-]} = K_2' \qquad \text{(eq. b)}$$
Second dissociation constant of carbonic acid.

$$[H^+]\,[OH^-] = K'w \qquad \text{(eq. c)}$$
Solubility product of water.

$$[Alk]+[H^+] = 2[CO_3^=]+[HCO_3^-]+[OH^-] \qquad \text{(eq. d)}$$
[Alk] is in equivalents/liter all other concentrations are molal.

Also, the calcium concentration may control carbonate by the solubility reaction:

$$[Ca^{++}]\,[CO_3^=] = K_s' \qquad \text{(eq. e)}$$

Empirical results have shown that optimum conditions for calcium carbonate scale formation and protection are (43):

1. Calcium carbonate oversaturation of 4-10 mg/l.
2. Calcium and alkalinity concentrations of at least 40 mg/l.
3. pH range of 6.8 to 7.3.
4. Halogen plus sulfate/alkalinity ratio of less than 0.2, on a milliequivalent basis.

By knowing the pH, alkalinity, and calcium concentration, the saturation condition of the water may be determined by using Caldwell-Lawrence diagrams (35). Additions of calcium and carbonate alkalinity needed to meet the optimum criteria are calculated from these diagrams. An alternate approach (34), if adequate alkalinity exists in the water, involves empirically determining the saturation pH of the water and adding lime to achieve that value. A third alternative is to adjust the water to achieve a zero or positive number on the Langelier Saturation Index (SI) (29), defined in section 2. Saturation index correlations with observed corrosion and red water problems have been good but not completely consistant (12). Maintenance of the SI within one unit of zero is considered satisfactory to eliminate extensive corrosion problems (16).

Methods used to increase calcium, alkalinity, and pH in corrosive waters depends on existing water constituents and raw material procurement costs, including transportation (5). One method used with desalinization waters is to blend the process stream with a naturally hard water. Because the distilled water is deaerated and of low pH, this water may need to be aerated and limed to add necessary oxygen and raise the pH.

When carbon dioxide is inexpensive, it can be added to react with either lime or limestone to produce a calcium bicarbonate rich water. A concentrated solution is prepared in a split stream and blended into the entire flow. Additional lime may be needed to raise the pH of the water to obtain a zero Saturation Index. The use of pulverized limestone, ground to 80 mesh, is generally insufficient to produce effective stabilization because of the required contact time. A pH above 6.5 is seldom achieved, but this method is attractive if iron removal is also needed. Filtration through partially calcined dolomite will raise the pH to 8.0 to 9.0, but the cost, compared to lime, makes lime more attractive except in very small systems where simplicity of operation is paramount. In areas where alkalinity is >25 mg/l as $CaCO_3$, the preferred method is lime addition. Lime readily dissolves in water and is generally cheaper than limestone on the basis of equivalents of calcium (5).

Although the use of calcium carbonate corrosion control is widespread, best results are still based on empirical data. While the optimum guidelines have been set, variables of temperature, velocity, dissolved oxygen, and other dissolved solids also affect the process. A temperature increase will decrease the calcium carbonate solubility, causing a given water to be closer to $CaCO_3$ saturation conditions. Also, reaction rates will increase. In solid-liquid reactions, a 10°C rise will generally increase the reaction speed by a factor of two (29). Saturated water heated to boiling will dissociate bicarbonate ions to the corrosive free CO_2 and hydroxyl ions (23). Water velocity affects the boundary layer and hence the transport of corrosive or protective material to the surface. In general, velocities greater than one fps are needed to deposit a protective barrier. Higher velocities provide better coatings (33). Because the strength of the $CaCO_3$ film depends on the presence of ferric oxides, the maintenance of 5 ppm dissolved oxygen is recommended (5).

Corrosion in lead pipes can be controlled by calcium carbonate deposition (38). Again, the stability of $CaCO_3$ is regulated by adding calcium and/or alkalinity or adjusting the pH. If pH adjustment alone is used, enough hardness must be present to provide the necessary calcium carbonate. Patterson and O'Brien (38) have suggested that pH adjustment without sufficient carbonate and alkalinity may be detrimental due to the preferential formation of $Pb(OH)_2$. This compound is non adherent and is potentially toxic as are all lead carbonate and hydroxide solids. Also, intermittent monitoring may not be sufficient to detect its presence. In general, soft waters, which are not amenable to pH adjustment only, occur on the eastern seaboard and in the southeastern and northwestern portions of the United States.

Dissolved solids other than calcium and carbonate species influence the rate of $CaCO_3$ formation. An increase in salinity causes an increase in the solubility of calcium carbonate ($CaCO_3$ is about 500 times more soluble in sea water than in fresh water) and explains why brackish waters are unable to form protective pipe coatings (29). Divalent ions (Mg^{++}, $SO_4^{=}$) also increase the solubility of $CaCO_3$, probably due to the increased ionic strength where fewer calcium and carbonate ions would become available for interaction (15). Because of the change in concentration of ionic species after some deposition has occurred, it is not uncommon to experience excessive deposition in and near the treatment plant with lessened protection in outlying areas. It should also be noted that increasing calcium and alkalinity too far beyond the saturation point may produce excess deposition (scaling). This is not uncommon when alkaline waters are lime treated without recarbonation. Also, where chlorination is used as a disinfectant, a pH increase means a decreased HOCl (the most effective chlorine form in water) content. Thus, lime addition for corrosion control may necessitate increased chlorine doses for effective disinfection.

Lime is available commercially as quicklime or hydrated lime. Quicklime is purchased in granular form and contains at least 90 percent CaO, magnesium oxide being the primary impurity. Hydrated lime is a powder containing approximately 68 percent CaO. Both forms of lime are dissolved into a 5 percent slurry prior to addition to the water system. Alkalinity is often applied in the form of soda ash (Na_2CO_3), a greyish-white powder containing about 98 percent sodium carbonate.

Lime addition requires the use of a slaker for quicklime while hydrated lime is often prepared in a tank with a turbine mixer. The slaker uses a gravimetric feeder to introduce the lime into a mixing chamber, where the proper amount of water is added to produce the desired slurry concentration. The ratio of water to lime is about 5 to 1, and pH controls that compensate the water to lime ratio in relation to changes in water quality or lime purity are available. Regulators protect against excessive temperatures resulting from the chemical reaction:

$$CaO + H_2O \rightarrow Ca(OH)_2.$$

A grit remover is used to remove coarse material prior to the solution being pumped to the slurry feeder. The feed rate into the water system is controlled by an automatic pH and flow control system (52).

One carbonate process that is gaining popularity is the low-carbonate method. Recently implemented in Bennington, Vermont, and soon to be used in Seattle (see section on Case History), this method raises the pH of the corrosive water to 8-8.3. Adding small amounts of alkalinity causes the formation of insoluble carbonate salts on pipe surfaces. Effective corrosion control is achieved without drastically altering the chemical makeup of the water. Results in Bennington showed an 82 percent corrosion reduction in lead and an 80 percent reduction in copper pipes (39). This method is also effective with galvanized surfaces.

Sodium Silicate

Sodium silicate, originally used to prevent metal solubilization in lead pipes, has been used for rust inhibition for over 50 years (48). Water conditioning by addition of sodium silicate is primarily applicable to galvanized piping where it is used to curtail existing red water problems and prevent corrosion, especially in hot water pipes. Sodium silicate is non-toxic and has the ability to control pre-existing conditions.

Perhaps the first consideration for using sodium silicates for corrosion control in an entire utility was to prevent the solution of lead from lead pipe in 1922. It was noted in this work that the corrosion of ferrous materials was reduced (48). Since that time, the use of sodium silicates has been attempted with some success over a wide range of applications (44)

The mechanisms of corrosion control with the addition of sodium silicate is thought to be the formation of a two-layered protective film between the material surface and the corrosive water. From results of laboratory studies, Lehrman & Shuldener determined that in dilute sodium silicate solutions, silica will exist in equilibrium between its ionic and collodial states (30). At low concentrations, such as those required for corrosion control in potable water systems, this equilibrium is attained very rapidly, if not instantaneously. The presence of silica in a zinc/iron system tends to make the zinc anodic to iron and the zinc reacts with water causing the formation of zinc hydroxide. The positively charged zinc hydroxide reacts with the negatively charged collodial silica from the water and silica is absorbed producing an amorphous silica (gel) deposit or layer capable of enmeshing compounds of iron, calcium, magnesium, and organic matter above a layer of metal corrosion products (30). In low alkalinity waters, this deposit is basically hemimorphite $[Zn_4Si_2O_7(OH)_2\ H_2O]$ with some ferrous or calcium silicate depending on whether the water is soft or hard (28), (11). In waters of higher alkalinity, especially at higher temperatures, Shuldener & Lehrman report that the zinc-iron potential can be reversed and the iron becomes anodic to the zinc causing the formation of ferric hydroxide (45). Although not as effective as zinc hydroxide, ferric hydroxide will also remove silica from water forming the amorphous silica layer.

Shuldener & Lehrman explain that when small amounts of silica are added to systems containing bicarbonate, especially at higher temperatures, two competing reactions can occur (45). The presence of silicate tends to make the zinc anodic to iron and the bicarbonate tends to do the reverse. The zinc corrodes to form a zinc hydroxide corrosion product which adsorbs silicate. As the silicate is removed and the concentration lowered, its effect is lowered and iron corrosion products are formed by the influence of the bicarbonate concentrations. Because the iron is not as effective at removing silica and because the silica concentration is now much lower, some rust can appear.

Shuldener & Lehrman conducted laboratory studies to investigate temperature, pH, and bicarbonate effects on the effectiveness of silicate for corrosion control (45). They simulated a galvanized pipe carrying a water at approximately 1.9 fps by rotating a pipe in water solution through which CO_2-free air was bubbled. They determined that the corrosion rate, as observed from rust formation, increased as the temperature increased from 72°F to 160°F, but that the addition of sodium silicate in the solution would act as a corrosion inhibitor and decrease the corrosion rate. From the laboratory studies on pH effects, Shuldener & Lehrman observed that in a solution containing 8.5 mg/l SiO_2 and 14 mg/l bicarbonate, decreasing the pH from 8.5 and 8.0 to 7.5 and 7.0, respectively, resulted in reducing the corrosion rate. Similar results were obtained in waters containing 8.5 mg/l SiO_2 and 54 mg/l bicarbonate when the pH was decreased from 8.5 and 7.0 to 6.5. PH adjustment was with dilute H_2SO_4 but specifics of the pH measurements in relation to the heating of the water or temperature corrections were not presented.

From their experiments it was shown that the presence of bicarbonate has an accelerating effect on the rate of corrosion. As is noted, as the pH increases in the range of 8 to 9, the concentration of bicarbonate decreases which implies that the effect of bicarbonate is closely associated with the pH of the solution (45). From their studies they concluded that bicarbonate has a very strong influence in causing reversal of potential with a resulting rust formation at 160°F (45).

Lane et al, conducted laboratory tests to investigate the effects of pH at various silica levels on the corrosion of galvanized steel at a domestic hot water temperature of 140°F. Their tests were conducted using a water with a pH range of 7.2 to 9.0, a hardness concentration of 100 mg/l (as $CaCO_3$) an alkalinity concentration of 35-55 mg/l and a velocity of 1.5 fps. Silica levels were varied from 10.0 mg/l to 20.0 mg/l. From results of their experiments, they determined that initially, the higher concentration of 20 mg/l silica was more effective than the lower concentration of 10 mg/l silica for controlling corrosion. However, after a sufficient period of time (possibly 60 days), Lane et al concluded that the effects on corrosion control is essentially the same at both levels of treatment indicating that there is no advantage to using the higher application rates (28). In both cases, however, corrosion control was most effective at the higher pH (8.5-9.0) condition. From the results of their tests, Lane et al state that the optimum silicate treatment appears to be a complement of pH and silica dosage, i.e., lower pH requires higher SiO_2 dosage and vice-versa, and is apparently influenced by water quality factors as calcium, magnesium, alkalinity, chloride, sulfate, and pH (28). Their experiments did not attempt to evaluate the effects of these water quality factors.

Sodium silicate dosages are independent of naturally occurring silica in the water and there are no specific concentrations recommended for the various conditions of water quality (51). As a general rule, however, an average concentration of 2 to 8 mg/l and possibly up to 12 mg/l SiO_2 is sufficient to maintain corrosion control in a system once a protective film is established. This inhibitor has been found to be particularly useful in waters with very low hardness, alkalinity, and pH < 8.4, and is more effective under higher velocity flow conditions. The application of sodium silicate requires the use of solution feeders, small positive displacement pumps that deliver a specific volume of chemical solution for each piston stroke or impeller rotation. The two general types of solution feeders are diaphragm and plunger metering pumps, although some rotary pumps may be used as positive displacement pumps as well. Both the diaphragm and plunger pumps may be controlled manually by adjusting the stroke length or rate of reciprocation, or they may use an automatic control unit that regulates stroking in proportion to water flow (52).

Inorganic Phosphates

Polyphosphates have been used to control calcium carbonate scale buildup in water treatment plants and irrigation systems since the 1930's. Presently, both polyphosphates and orthophosphates may be used for scale inhibition or corrosion control. The effectiveness of these chemicals is a function of flow velocity, phosphate concentration, temperature, pH, and calcium and carbonate levels.

Both ortho- and polyphosphates (especially tri-, pyro-, and higher polyphosphate anions) are known to form complexes with a number of metal ions, including calcium, iron, and lead (49). The presence of larger amounts of polyphosphates has been blamed for assisting iron and lead uptake from pipe surfaces in laboratory situations by upsetting local metal-ion equilibrium through complexation. When concentrations generally less than 10 mg/l of polyphosphates are introduced into a flowing water, however, they have a tendency to form a thin film on the metal pipe surface that protects the metal from further corrosion. This film will also adhere to calcite crystals, preventing further growth. In this way, a water supersaturated with calcium and carbonate can be prevented from scaling. The minimum concentration of polyphosphates that will prevent crystal formation for a particular water is called the threshold level. Subthreshold concentrations will produce distorted calcite crystals (33).

The threshold concentrations of polyphosphates, usually added as sodium hexametaphosphate, is pH dependent in calcium and carbonate containing waters due to the pH dependency of $CaCO_3$ deposition. Successful red water control has been achieved in waters that had unsuccessfully responded to lime teatment. In Little Rock, Arkansas, Uniontown, Pennsylvania, and Newport, Rhode Island, polyphosphate addition to lime treated waters with initially high pH ($\geq$9.0) resulted in corrosion abatement at polyphosphate concentrations of 1.0 to 2.0 ppm. However, the red water problems in Nitro, West Virginia, persisted in the lime treated water even at 10, 5, and 1 ppm polyphosphate concentrations.

Phosphates may be used to control corrosion in lead pipes, but because corrosion control in lead pipes is primarily interested in preventing lead being carried into the water as opposed to the pipe deterioration, the phosphate concentration must be low enough not to form soluble lead complexes (21). Corrosion protection by addition of sodium hexametaphosphate is best a pH $\leq$ 7.0 (9). Above this pH, and in the absence of phosphates, a lead-carbonate film will deposit on the surface and protect the pipe. If polyphosphates are present, the formation of this film is retarded and more lead may enter the water than would occur if either the addition of polyphosphates at low pH or the existence of a high pH alone were maintained. Effective corrosion control in lead pipes at pH below 7.0 has been achieved with sodium hexametaphosphate concentrations at or below 2 mg/l (21). These experiments also showed that lead levels at pH 8.9 were equivalent with or without polyphosphate addition and lower than those achieved at pH 7.0 or below with polyphosphate addition at low alkalinity.

Other pipe surfaces respond differently to polyphosphate corrosion control (9). The staining of plumbing fixtures due to the dissolution of copper or the components in brass has been lowered but not stopped by polyphosphate addition.

Aluminum protection has been obtained in laboratory tests, especially at low pH values. Zinc corrosion has also been controlled by 2 ppm polyphosphate addition to the water. At least two separate cases have been reported where the protection of galvanizing was excellent. Specifics on these tests, however, were not given (9).

One report of copper corrosion control by hexametaphosphate addition (6) reported that early morning copper concentrations were reduced from an average 4.8 to 5.5 ppm to an average of 2 ± 0.2 ppm copper. The pipe was 12 to 14 month old house lines in a district in England. Initial composition of the water was not reported. Hexametaphosphate addition relieved complaints of blue water and emetic reactions to use of the water that had stood in the pipes overnight.

A process involving orthophosphate addition has been developed (36, 27). The process involves the formation of a zinc orthophosphate, $Zn_3(PO_4)_2$, in the pipeline and its subsequent precipitation as an insoluble zinc orthophosphate film. This reaction involves adding zinc sulfate, sulfamic acid, and monosodium orthophosphate to the water:

$$3ZnSO_4 + 2HNH_2SO_3 + 2NaH_2PO_4 \rightarrow Zn_3(PO_4)_2 + 2NaNH_2SO_3 + 3H_2SO_4$$

Because zinc solubility, even in the presence of $PO_4^{\equiv}$, is pH dependent, an initial application of zinc is empirically maintained at 2 to 3 ppm.

After the coating is formed, in about 3 weeks, the zinc is reduced to 1 ppm. In highly alkaline waters, between 0.5 and 1 ppm sodium hexametaphosphate may have to be added to prevent $CaCO_3$ precipitation. This is because $CaCO_3$ weakens the $Zn_3(PO_4)_2$ film, decreasing its anti-corrosive efficiency. The results of one test using this procedure is presented in Tables 37 and 38.

TABLE 37. ANALYSIS OF A NEW JERSEY WATER

hardness, ppm	96
sulfate ($SO_4^{=}$), ppm	44
pH	7.0
M.O. alkalinity, ppm	52
TDS, ppm	150
Langelier Index	1.1

TABLE 38. 63-DAY CORROSION TEST ON CAST IRON USING TREATED NEW JERSEY WATER

Coupon	Exposure (days)	Corrosion Rate (mpy)	% Corrosion Reduction
Control	31	10.20	
Treated	31	8.24	19
Control	63	10.77	
Treated	63	5.24	51

Source = (27).

Other recent tests (26, 38) on the ability of zinc orthophosphate to prevent corrosion in lead pipes has presented negative results. Karalekas et al added zinc orthophosphate to Boston water (low alkalinity and hardness, pH < 7.0) for a six-month period and could not reduce the lead levels to the 0.05 mg/l standard. Patterson and O'Brien immersed lead coupons in stagnant water and determined that lead corrosion could increase from the use of zinc orthophosphate. The pH conditions during their short term test varied from 7.24 to 9.13. The long term test pH was held between 6.52 and 6.82 and showed a 60% increase in soluble lead content in the treated water. Murry (36) reported that zinc orthophosphate is insoluble in water so his process was the in situ formation of zinc orthophosphate during flowing conditions. However a Ksp of 1×10^{-32} has been reported for zinc orthophosphate (4) and others (18) have reported that orthophosphate can substantially reduce lead levels in waters of pH 7-8.2 with low alkalinities and carbonate levels. Because of these inconsistant findings, more research is needed on this corrosion control mechanism.

Other organic and inorganic phosphate-phosphonate corrosion inhibitors are used for industrial scale control but are not applicable to potable water systems. Also, the possibility of eutrophication in lakes and streams that ultimately receive the water has discouraged at least one city from using inorganic phosphates for corrosion control. The critical level for algal growth has been established as somewhere near 0.01 mg/l (42), and it was believed that the wastewater treatment plants might not be able to reduce the phosphorous content to this extent.

In summation, several important factors must be addressed prior to the use of inorganic phosphates for corrosion control in any specific water system. The effectiveness of polyphosphates, usually added as sodium hexametaphosphate, is greater with increasingly turbulent velocities, and flow velocities of 2-5 fps and above are not continually experienced in all parts of any distribution system (51). Under stagnant or nearly stagnant conditions, such as service lines, polyphosphates will not be effective. In waters saturated with calcium carbonate, polyphosphates will prevent $CaCO_3$ deposition, and larger amounts of polyphosphates may assist in iron and lead concentrations through complexation. Polyphosphates have been shown to alleviate "red water" in many, but not all, situations where the iron content was originally in the water and where the iron was a result of pipe corrosion. Polyphosphates can also prevent lead release into the water by forming a thin film of complexation compounds across the lead surface. Effective polyphosphate concentrations reported are usually $\leq$ 2 ppm, but an initial concentration of up to 10 mg/l for up to three weeks has been used to produce an initial film. Orthophosphates have produced both positive and negative results for lead control and more clarifying research is needed.

Polyphosphate addition is by use of solution feeders as discussed in the silicate section. Concentrated solutions are mildly corrosive, so stainless steel is often used for the dissolving tanks, baskets, and the liquid end of the chosen pump. The positive displacement pump(s) are generally selected from accuracy, durability, capacity, corrosion resistance, and pressure capability requirements, and most manufacturers have designs to accommodate the specific need.

Miscellaneous Methods

Other corrosion control methods are applicable to more specific situations. In instances where high sulfate concentrations are producing corrosive sulfides, which tend to accelerate the anodic dissolution of iron (43), the sulfate reducing bacteria responsible for the sulfides may be eliminated by maintaining proper chlorine residuals in the water system. This problem should not occur under normal conditions where disinfection procedures and natural aerobic conditions occur.

Dissolved oxygen removal will curtail corrosion. Deaeration may be accomplished by applying a pressure vacuum, heating and degasification, or deactivation. Deaeration is too expensive to be considered a viable corrosion control for municipal water systems.

Cathodic protection, previously a common corrosion inhibiting method in water tanks, occurs when electrons are supplied to the metal surface being protected, decreasing that metal's tendency to oxidize. Electrons may be supplied by a direct current or by a sacrificial anode. The latter consists of a metal higher in the electromotive series than the protected metal and is, therefore, preferentially corroded. Examples of a cathodic protection are magnesium rods in hot water heaters and the zinc used to galvanize steel.

ECONOMICS

The economics of corrosion abatement is often simplified to a comparison of annual costs incurred by implementing additional chemical treatment to the water supply and/or the increased cost of pipe lining versus the annual costs for replacing distribution pipes (46). Increased pumping costs due to reduction in the hydraulic efficiency of corroded piping and increased costs due to shortened pipe or appliance life are sometimes, but not always, included in cost analysis. However, health and aesthetic effects and possible increased cost due to excessive deposition (scale) are often ignored.

Benefit/Cost Analysis

In Benefit/Cost analysis, a price is determined for each aspect of corrosion control and the sum of the annual costs for imlementation of the abatement method is compared to the sum of the annual "lack of costs" experienced by the utility or by the user and the utility. Costs for implementation of the corrosion control are presented in the next sections and reflect construction, materials, chemicals, and labor cost as well as intangibles such as public acceptance and relative economy of the area. Benefits are harder to quantify, especially in terms of pricing the "lack of costs" to be incurred by the consumer.

User benefits may be classified as directly economic, aesthetic, or in terms of health. The directly economic savings results from extended service lives of piping, fixtures, and appliances, as well as lessened damage from water leaks, and are generally formulated by first determining the extent of corrosion-based annual costs and subtracting annual costs for similar repairs experienced in similar areas practicing corrosion control. Methods used to determine the extent of problems caused by corrosive waters include a review of customer complaint records, the use of questionnaires, corrosion rate testing, examination of plumbing pipes, and water quality monitoring in residences. From data collected, a service life for waterheaters, pipes, faucets, shower heads, appliances, etc. is determined, and annual cost for maintenance and repair or replacement is figured. Unfortunately, the prices determined are applicable only to the individual distribution system samples supplying the data as results from similar areas using the same water source have produced drastically different costs (8). Also, attempts to correlate water quality parameters with corrosive effects in terms of economics have been poor (37, 8). One study (37) tried to correlate the corrosive potential with the Saturation Index, the Ryznar Index, and the chloride plus sulfate concentration and ended up finding the greatest correlation ($r = 0.33$) between TDS and houses that had to replace interior piping. No positive correlation was found between TDS and replacement of faucets, shower heads, or toilet flushing mechanisms. Whereas that study assessed a penalty cost of 18¢/m^3 for users of Colorado River water in Southern California another study assessed a 4.5¢/m^3 value for the same water source in the same area (8). (These prices included the cost of soaps and detergents and bottled water costs as well as corrosion-induced costs) Both studies were conducted by questionnaires, but problems with this type of survey were demonstrated by the latter study. For example, substantial differences in service life estimates were found between plumber and repair shop responses as compared to consumer responses. It was also noted that increased water hardness caused greater use of home softening units that may increase the corrosiveness of waters by increasing conductivity and decreasing the Saturation Index. Results of testing designed to substantiate this claim were, however, inconclusive as seen from the results of copper testing in five residences:

	influent	after softening but prior to contact with plumbing	after contact with plumbing
Copper piping	30	440	40
" "	20	80	110
" "	130	260	530
Galvanized iron piping	10	5	<5
" " "	80	50	320

TABLE 39

Copper Concentrations (ug/l) in Domestic Waters

(10)

An example of the computed savings per residential unit resulting from the recommended corrosion control measures in Seattle (see section 6 - Case Histories) is presented in Table 40. The annual plumbing deterioration cost savings is estimated at $1,700 or $7.50 per year per residential unit. Table 40 indicates that the savings for a specific unit depends on its location, age, and type of plumbing. The savings to older homes, whose piping is presently substantially deteriorated would be reduced, and the control measures should minimize the rate of plumbing system corrosion in the future. (25)

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TABLE 40
(1978 Prices)
Source (25)

COMPARISON OF ESTIMATED ANNUAL COSTS AND SAVINGS
OF CORROSION RELATED DETERIORATION
WITH AND WITHOUT CORROSION CONTROL TREATMENT

		SOUTH AREA CEDAR RIVER				NORTH AREA TOLT RIVER			
Residential Category	Plumbing Type	Number of Units	Estimated Annual Cost/ Unit W/O Treatment	Expected Annual Cost Savings/Unit Provided By Treatment	Expected Annual Cost/ Unit W/ Treatment	Number of Units	Estimated Annual Cost/ Unit W/O Treatment	Expected Annual Cost Savings/Unit Provided By Treatment	Expected Annual Cost/ Unit W/ Treatment
Single Family & Duplex									
All Units	Galvanized Steel	62,051	$39.35	$10.40	$28.95	52,551	$48.50	$7.20	$41.30
Units built 1971-75	Galvanized Steel	166	7.60	6.35	1.25	176	17.10	7.55	9.55
All Units	Copper	14,183	3.95	3.90	0.05	15,151	5.10	4.60	0.50
Units built 1971-75	Copper	664	7.05	6.95	0.10	880	7.10	6.70	0.40
Multi-Family									
All Units	Galvanized Steel	40,700	25.30	8.75	16.55	12,988	32.90	6.45	26.45
Units built 1971-75	Galvanized Steel	410	4.70	3.90	0.80	152	12.45	6.45	6.00
All Units	Copper	16,812	2.90	2.85	0.05	8,720	3.20	3.15	0.50
Units built 1971-75	Copper	1,720	4.90	4.85	0.05	760	4.80	4.60	0.20

Health and aesthetic problems resulting from corrosive waters are definable but hard to quantify economically. Aesthetically, iron concentrations may present turbidity and color (red water) problems; the drinking water limit for zinc is based on taste tests; dissolved copper may cause a blue green stain on porcelain where soap residues accumulate; and manganese may cause brown-black staining. In terms of health, lead and cadmium may be toxic in low levels, and other heavy metals may be leached from pipes and solders. Furthermore, causes of the correlation between increased cardiovascular disease and soft waters have not been positively identified but may result from either the role of the bulk mineral content (Ca, Mg, Na) of hard waters or the metal constituents in soft waters resulting from its corrosive nature (24). While cost figures have not been placed on the aesthetic problems, it is estimated that the difference in cardiovascular mortality, between corrosive and non-corrosive waters is 52 deaths/100,000 population annually, which translates to 47,000 avoidable deaths attributable to a lack of corrosion control, and an income loss to the U.S. of $3 billion annually (24).

Trends and Costs of Mechanically Applied Linings and Coatings

Cast iron and ductile iron pipe, composing over 76% of the pipe used in U.S. water supply distribution systems serving over 2,500 people, is exclusively lined with cement mortar. Steel pipe, at 6%, is increasingly being lined with epoxy. Although epoxy is more expensive than coal tar, the benefit of a high smoothness coefficient, a lack of having to control coal tar enamel application fumes, and possible adverse health concerns arising from the use of coal tar based linings, have caused this increased epoxy usage. There are two manufacturers of hot applied coal tar enamel for potable water system lining in the United States with total 1976 coal tar enamel sales of $1,500,000. One company estimated that half of the steel pipes installed by the water supply industry were coal tar enamel lined.

The extent of use of various linings and coatings for water tanks is not well defined. The extremes of material use estimates reported by various vendors and manufacturers is shown in Table 41. As can be seen, a wide range of discrepancy exists.

TABLE 41.

EXTREMES OF VARIOUS ESTIMATES OF USE OF TANK LININGS AND COATINGS

COATING	EXTREMES OF ESTIMATIONS (10 FIRMS REPORTING) OF % OF NEW WATER TANKS LINED WITH A GIVEN COATING NATION-WIDE
Vinyl	47.5 – 90
Epoxy	6 – 50
Coal Tar	0 – 90*
Other	0 – 17

* 0-19% reported on all estimates except one firm indicated 90% (19)

Besides manufacturer's preferences, regional preferences exist in relation to water tank linings as seen in Table 42.

TABLE 42.

REGIONAL PREFERENCE FOR WATER TANK LININGS

(compiled from (19))

CITY/STATE	PREFERRED LINING/SPECIFICATION FOR STEEL TANKS
Seattle	~100% Coal Tar Enamel
Atlanta	Coal Tar Enamel
Houston	Vinyls and Epoxys Used
Virginia	Coatings containing coal tar, vinyl or bituminous material not approved.
Baltimore	Chlorinated Rubber
California	No longer uses coal tar enamel due to possible health affects

The cost of applying linings to water tanks varies widely and is a function of the application method, surface preparation, cost of labor, and intangibles such as regional competition and local materials preference. Table 43 presents the extremes of cost estimates for the linings discussed in the text.

Costs of Corrosion Control by Chemical Applications

After the chemical constituents of a corrosive water have been identified, and potential control mechanisms are listed, the cost of treatment for each method must be determined. Because local construction, materials, chemical, and labor costs, along with intangibles such as the local economy and water quality demands, influence cost estimating, this section should be regarded as a general overview. Where possible, weight units are used because prices quoted are apt to reflect temporal and regional values that may or may not differ from current prices. Brand names used are those reported from the articles cited and do not constitute an endorsement of the product.

Sodium silicate has been effective in reducing plumbing repair costs when used to treat water used in groups of buildings or housing developments (44). This additive is more cost effective when used in very soft, low alkaline waters, especially when compared to the use of lime, sodium hydroxide, and/or soda ash. To obtain the 8 ppm silica concentration regarded as the minimum level needed for corrosion control, a 28 ppm sodium silicate solution, equivalent to 232 pounds of solution per million gallons of water must be used (48). The cost of equipment needed is that of a solution feeder. Prices vary depending on the size, type (diaphragm or plunger metering pumps), and manufacturer; and selection is usually based on accuracy, durability, capacity, corrosion resistance, and pressure capablity.

The cost of using polyphosphates is seen in a 1966 study by the city of Richmond, Virginia. They compared the use of lime, Calgon brand metaphosphate with lime, and TG-10(a Calgon phosphate composition) with lime to stabilize their corrosive waters (7). Empirical tests coupled with manufacturer's data indicated that corrosion would be controlled using either 2.0 ppm Calgon or 1.25 ppm TG-10, each with a reduced lime consumption. An additional capital cost ($3000) would be required for the polyphosphate addition and the 1966 costs for the use of TG-10 plus lime, Calgon plus lime, and lime would have been $3.08, $2.35, and $1.00 per MG respectively. The report recommended the use of TG-10 based on lower pipe line maintenance costs, reduced valve and meter repair costs, and lower pumping costs from increased pipe diameters expected to result from reduced scale formation.

The additional equipment required for the TG-10 and Calgon systems included a ½ HP stainless steel Simplex pump (0.0-0.5 gal/min), two 400 gallon stainless steel tanks, two 5-cubic foot stainless steel dissolving buckets, two agitators (½ HP motor, 3-three blade propellers), one Simplex pump assembly, two electric timers, and one switch. Materials, based on a 40 MGD flow, were 2000 lbs lime; 400 lbs lime plus 717 lbs Calgon; or 400 lbs lime plus 440 lbs TG-10 to be used daily.

TABLE 43

COST ESTIMATES (19)

COATING	SURFACE PREPARATION $/Sq. Ft.	MATERIALS $/Sq. Ft.	APPLICATION $/Sq. Ft.	INITIAL COST* $/Sq. Ft.	SERVICE LIFE YEARS	COST EFFECTIVENESS $/Sq. Ft./Yr.
Coal Tar Enamel (Hot)	.40- .50	.10-.15	.30- .60	.94-2.00	20-50	.019-.100
3 Coat Vinyl	.47-1.00	.11-.22	.16- .50	.95-1.11	8-23	.048-.139
Metallized Zinc	.80-1.65	.50	1.15-1.75	2.45-3.90	40-50	.049-.098
4 Coat Vinyl	.24-1.00	.09-.20	.09- .21	.55-1.21	8-23	.053-.144
Chlorinated Rubber	.30- .75	.05-.17	.15- .50	.50-1.14	6-15	.055-.190
Coal Tar Paint (Cold Applied	.30- .75	.13-.25	.30	.73-1.30	12-15	.055-.083
Coal Tar Epoxy	.30- .75	.15-.20	.25- .30	.75- .95	10-14	.068-.075
2-Component Epoxy	.30- .80	.15-.50	.16- .70	.90-1.95	10-15	.060-.115
Asphalt (Petropoxy)	.50-1.00	.24	.30- .50	1.24-1.34	15	.083-.089
Wax	.12	.04	.29	.35- .45	4- 5	.088-.090
1-Component Epoxy	.24- .80	.06-.25	.16- .50	.47-1.50	10	.086-.115
Asphalt (Inertol #49)	.30- .75	.10-.11	.30	.70- .91	6	.117-.152
Phenolic	.30- .75	.11-.13	.16- .50	.77-1.11	4- 6	.185-.193
Zinc Rich Paint	.80-1.00	.25	.05- .15	1.10-1.40	5	.220

*Initial costs are as reported and may not include figures reported in surface preparation, material, or application columns.

Estimates were obtained from published literature, paint supplies, engineering consultants, and painting contractor costs were calculated from the 33rd edition of Building Construction Cost Data, 1975, Robert S. Means Company, and the Estimating Guide of the Painting and Decorating Contractors of America, 10th edition, 1977-78.

Relative costs of calcium carbonate stabilization are presented in a 1971 report on the pacification of product water from a distillation plant (5). Costs of adding 40 ppm (as $CaCO_3$) of calcium bicarbonate to the water are presented for the use of lime (CaO) and CO_2, limestone and CO_2, calcined dolomite and CO_2, and limestone and H_2SO_4 for both 10 MGD and 50 MGD flows. The capital costs of the storage bins, dust filter, slaker unit, mixers, slurry feed pump, recarbonator, aerator, instruments, etc. were $110,000 and $357,000 for the 10 MGD and 50 MGD flows and salary related costs were $27,000 and $68,000 per year, respectively. These costs were essentially the same for all processes investigated. Chemical prices cited were a reflection of shipping distances, especially in relation to the transportation charge of powered limestone, and the method of contracting for liquid CO_2 that may vary the CO_2 price by a factor of two. The 1971 prices given were:

Lime	$30/ton
Limestone	15/ton
Calcined Dolomite	150/ton
Liquid CO_2	50/ton
H_2SO_4 (93%)	23/ton

Chemical costs in 1971 dollars per 1000 gallons are presented in Table 44.

TABLE 44

CORROSION CONTROL BY CALCIUM CARBONATE STABILIZATION

PROCESS	COST $/1000 GAL	CAPITAL AND LABOR		CHEMICALS	TOTAL COST	
		10 MGD	50 MGD		10 MDG	50 MGD
Lime and CO_2		.89	.45	1.12	2.01	1.57
Limestone and CO_2		.89	.45	.82	1.71	1.27
Dolomite and CO_2		.89	.45	.95	1.84	1.40
Limestone and H_2SO_4		.89	.45	.98	1.87	1.43

from: (5) (1971)

Although these costs reflect 1971 prices, it is significant to note that in instances where limestone is half as expensive as lime and one tenth as expensive as calcined dolomite, and 93% H_2SO_4 is half as expensive as liquid CO_2, all on a weight basis, limestone and CO_2 would be the preferred process (5). Furthermore, a considerable savings would be realized if split stream treatment were used on part of the flow followed by blending with the remainder of the water.

Because of their applicability to calcium carbonate stabilization, cost curves (20) for lime feed systems and recarbonation via liquid CO_2 systems are included in this section. Construction costs for the lime feed system (Figure 36) are based on hydrated lime use up to 50 lb/hr and quicklime use at higher rates. The hydrated lime arrives in 100 lb bags, is introduced by feeder to a dissolving tank, and gravity fed to the point of application. The quicklime is stored in hoppers with a 30 day storage capacity (3 days if recalcination is used) located over the slaker. The slurry is gravity fed to the point of application. Operation and maintenace cost (Figure 37) do not include the price of lime and are based on $0.03/kw hour and $10/hour labor costs. Construction costs for liquid CO_2 system (Figure 38) include a 10-day storage tank, CO_2 vaporizer, a solution-type CO_2 vaporizer, a solution-type CO_2 feeder, injector pump, main header, diffuser pipes, and an automatic control system. Operation and maintenance (Figure 39) are based on $0.03/kw-hr. and $10/hr. labor costs. Costs on these curves are based on October, 1978 prices.

Estimates of the national cost of piping damage resulting from the distribution of corrosive waters range from $210 million annually (1975 dollars) (47) to $375 million annually (1976 dollars) (24). Estimates for the cost of implementing lime-addition corrosion control to stabilize these corrosive waters are from $20 million (47) to $27 million (24) annually. This simplified economic analysis does not account for the intangible benefits of elimination of red water, possible decreases in CVD mortality, or lessened pumping costs; yet, juding from the economics of pipe replacement alone, well-run utilities with corrosive waters can ill-afford not to implement control methods.

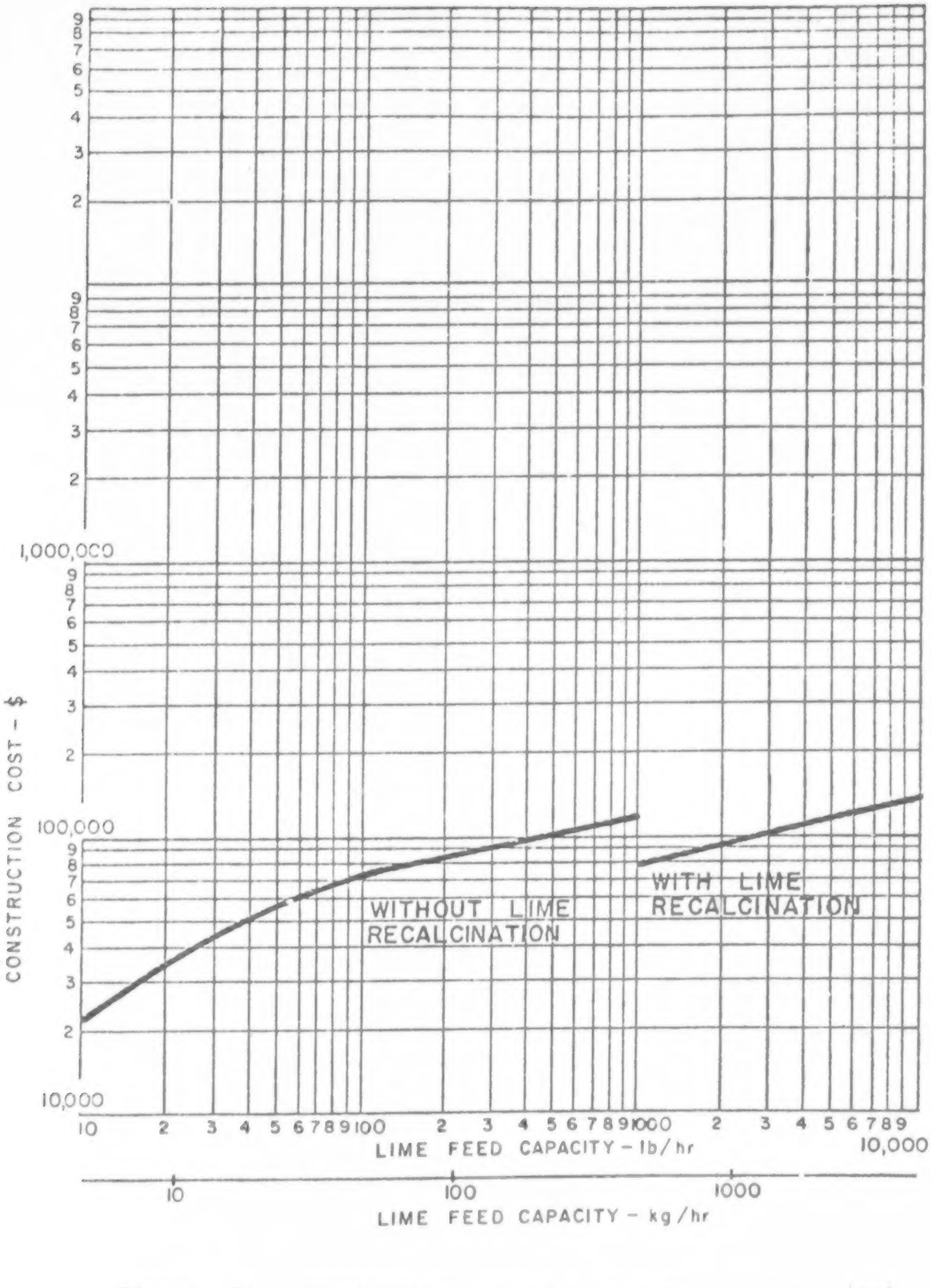

Figure 36. Construction cost for lime feed systems (20).

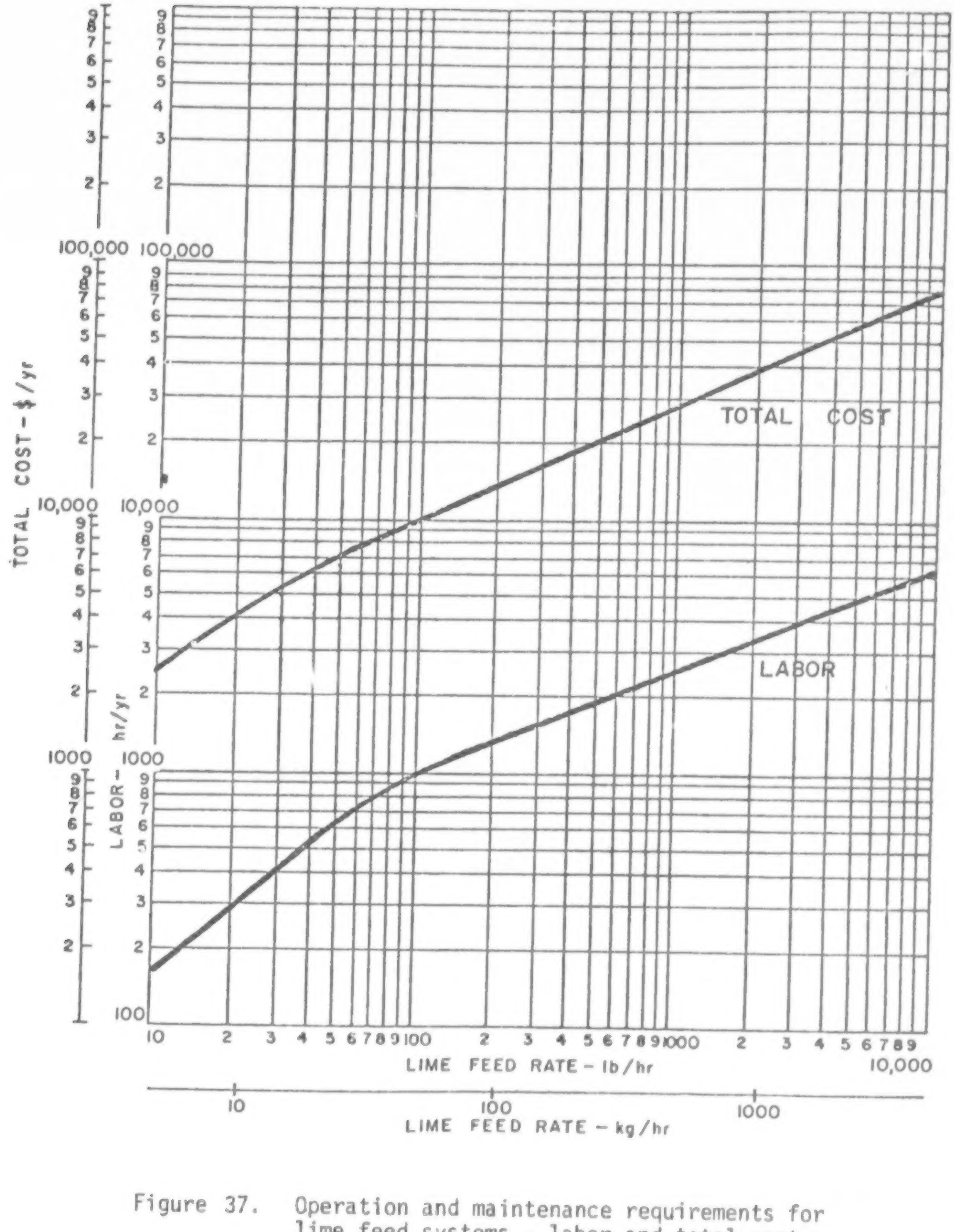

Figure 37. Operation and maintenance requirements for lime feed systems - labor and total cost. (20)

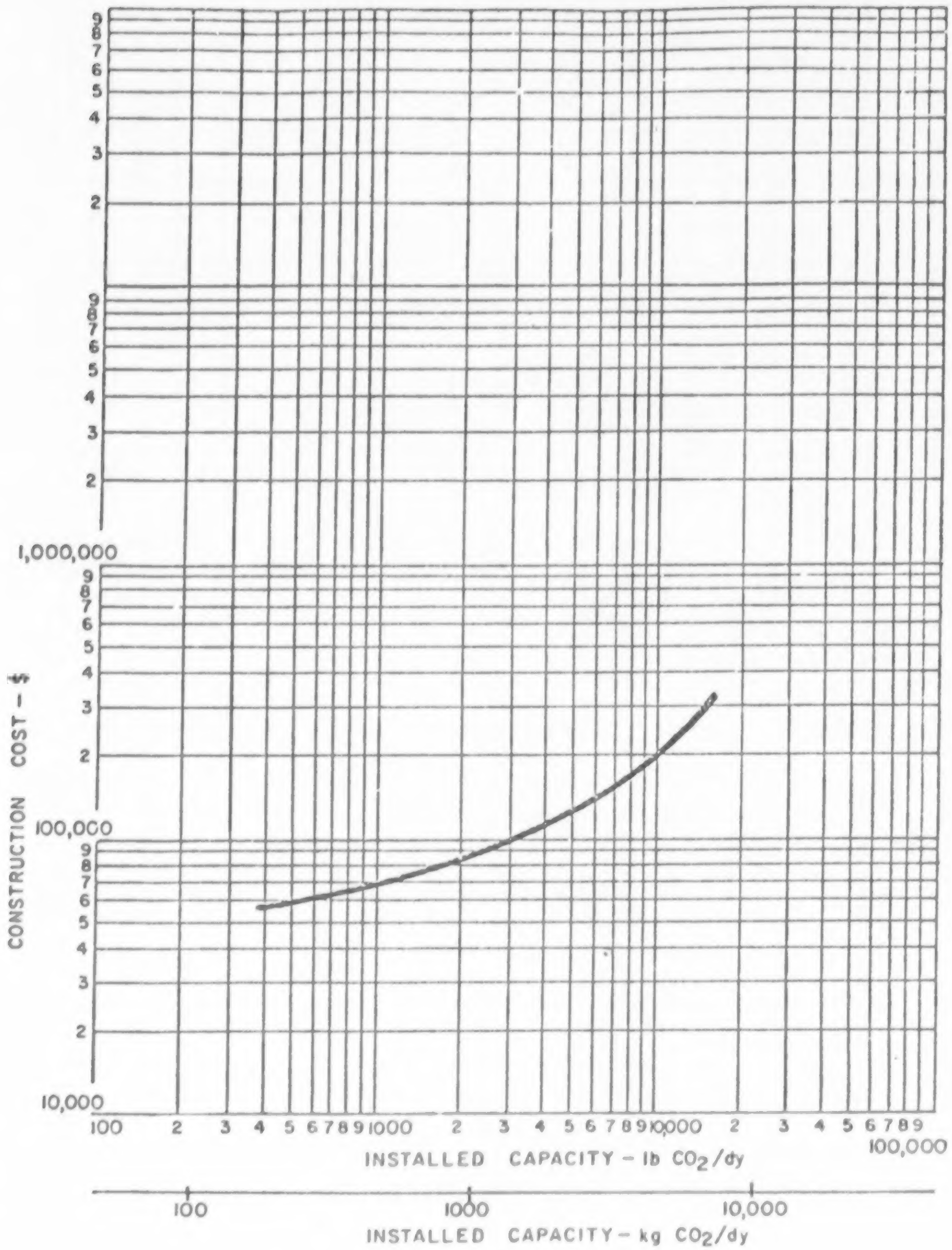

Figure 38. Construction cost for recarbonation - liquid CO_2 source. (20)

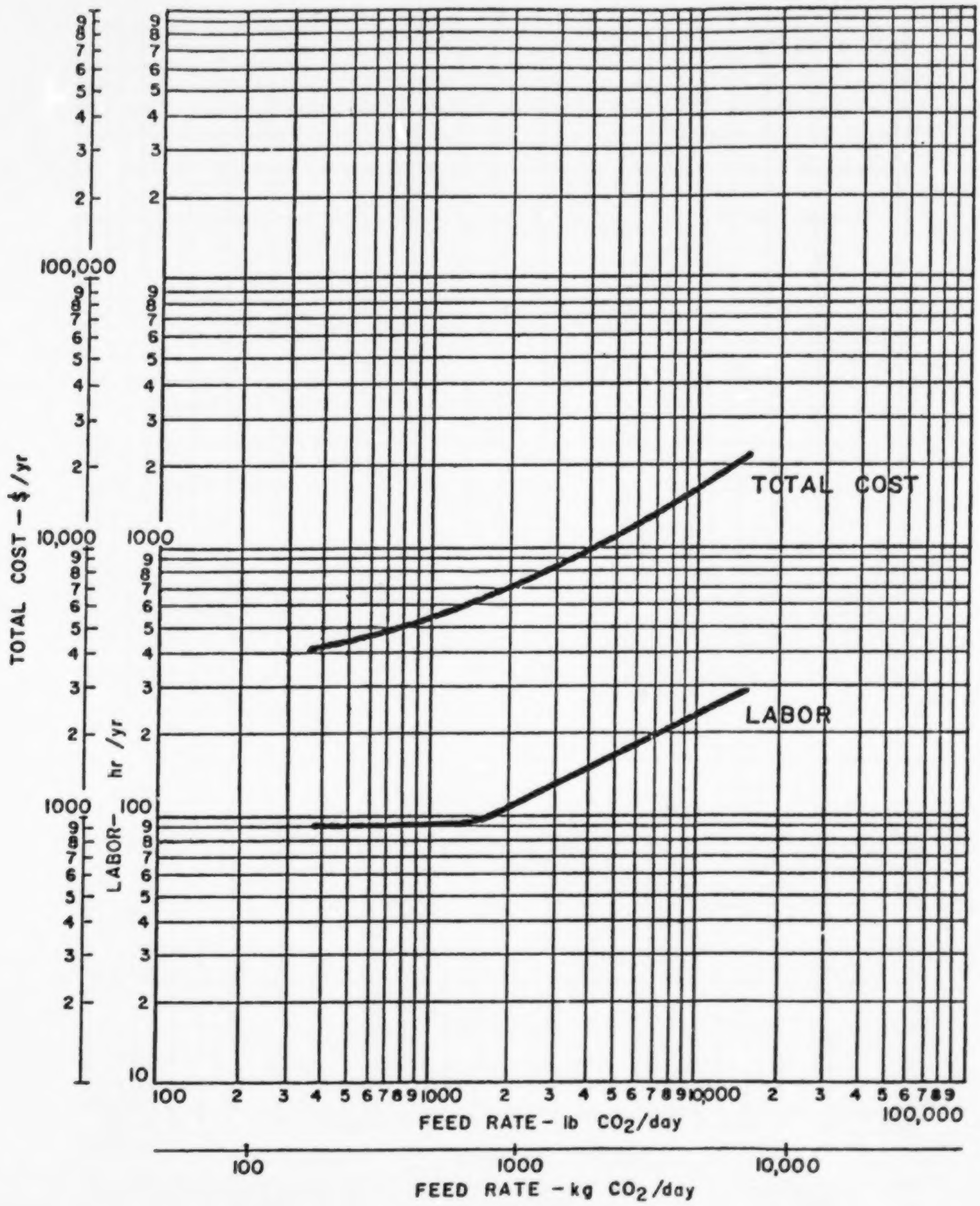

Figure 39. Operation and maintenance requirements for recarbonation-liquid CO_2 as CO_2 source - labor and total cost. (20)

CASE HISTORIES

Seattle

The Seattle Water Department has initiated a corrosion control program. Although the system is not yet operational, a review of the engineering involved in defining the problem and determining its solution demonstrates that corrosion control in the water works industry is an intricate and multidimensional process.

A slight increase in corrosion complaints occurred after Seattle started to use the Tolt River waters in addition to the existing Cedar River supply in 1964, but widespread complaints became common after 1970 when chlorination doses were increased, ammoniation was stopped to increase the free chlorine residual, and fluoridation with hydrofluosilicic acid began. Both water supplies are surface waters from rain and snow runoff in mountains east of the city. They are very soft, low TDS, low pH, highly oxygenated waters with some organics, principally tannins and lignins. Addition of free chlorine and fluorides caused this water to become excessively aggressive. Aesthetically based consumer complaints were followed by a water metals survey. Although metal increases in the distribution system mains were very low, lead, iron, zinc, and copper were being appreciably leached in buildings and residences. Lead, iron, and copper limits often exceeded federal limits when water was left standing in internal piping for as little as five hours. The predominant pipes in these structures were galvanized iron or copper. Lead increases were believed to be leached from soldering joints.

Because of adverse health and aesthetic reasons, as well as the expense water customers had to assume in maintaining residential plumbing, a study was initiated to determine the best applicable corrosion abatement process. Alternatives included:

1. Alternative disinfectant chemicals to replace gaseous chlorine.

2. Alternate fluoridation chemicals to replace hydrofluosilicic acid.

3. Blending ground water with the surface water to provide a less corrosive product.

4. Addition of corrosion inhibitors.

Alternate disinfection chemicals included calcium hypochlorite, sodium hypochlorite, and ozone. The first two would provide a less corrosive water but cost was two to six times greater than chlorine. Alternative fluoridation chemicals, sodium silicofluoride and sodium fluoride, did not provide effective corrosion control and were more expensive than the hydrofluosilic acid.

Blending ground water was deemed unfeasible because the only available ground water supply could be ecomonically used with only one of the two water systems. Additional costs of well construction, pipelines, and pumping stations coupled with the uncertainty of this means to affect a solution to the corrosion problem removed this alternative from consideration.

Corrosion inhibitors examined included lime, sodium carbonate, sodium silicate, sodium bicarbonate, caustic soda, and various phosphate compounds. The following are the results of the six alternatives selected for extensive testing.

1. Low-carbonate system. Lime and sodium carbonate were used to raise the pH to 9 and alkalinity to 10-30 mg/l. No calcium carbonate scale formed on pipe surfaces, excellent corrosion protection was provided for copper pipes and fair protection for galvanized and black steel pipes. However, the high pH attained raised questions about trihalomethane formation as the surface waters contained organic precursors and THM formation is known to be accelerated above pH 8.5. Also, the high pH was unstable in contact with air, decreasing by at least one pH unit within a day. Further testing with $NaHCO_3$ eliminated both of these problems, yet provided the same amount of corrosion protection.

2. Lime and zinc-orthophosphate. Although this method effectively eliminated corrosion, it was felt that the potential stimulant to algal growth from the phosphate and subsequent taste, odor, plugging of fine filters, and additional chlorine required did not warrant this as a desirable alternative.

3. Sodium silicate. Silica, added to a concentration of 10 mg/l, gave corrosion protection, but evidence of increased pitting rates coupled with an increased need to remove any silica added to the water by industries that were using the existing water without pretreatment made this alternative unattractive.

4.-6. These methods involved the carbonate method of corrosion control based on $CaCO_3$ precipitation. Each of these methods gave excellent protection for copper pipes and good protection for galvanized and steel pipes.

4. High pH, balanced lime and alkalinity. Adding 15-20 mg/l lime and 15-20 mg/l sodium bicarbonate produced a water with pH 8.8. Cost and THM formation possibilities made this alternative unattractive.

5. Moderate pH, balanced lime and alkalinity. By adding 35-40 mg/l lime and 55-60 mg/l CO_2 a water of about 75 mg/l calcium and alkalinity (as $CaCO_3$) and pH 8.3 was achieved. Cost of this method is excessive and the water would be classified as "moderately hard," imposing a much greater impact on industries that pretreat the water for hardness removal.

6. High alkalinity, moderate pH. By adding 10-20 mg/l lime and 65-130 mg/l $NaHCO_3$, a very soft water with pH 8-8.5 would result. Although attractive from a corrosion control and water quality aspect, the cost was excessive.

METHOD	ESTIMATED ANNUAL COST ($)
Low carbonate	510,000
Lime and zinc orthophosphate	430,000
Sodium silica	630,000
High pH, balanced lime and alkalinity	1,100,000
Moderate pH, balanced lime and alkalinity	1,700,000
High alkalinity, moderate pH	1,400,000

The low carbonate method using sodium bicarbonate was chosen because of its low cost and minimal affect on existing water and environmental quality. Additional sodium silicate will be added to the Tolt River system, bringing the silica level up to that of the Cedar River (7-9 mg/l) and providing additional corrosion protection. The mechanism of low carbonate control is a result of reactions between pipe material and carbonate, forming insoluble metal oxides that coat the pipe surface. Cost of the process and additional chlorine needed due to the increased pH is expected to be $1.13 per thousand gallons. Assuming a 100 gpcd water use rate, this amounts to $1.40/residence/year. The computed savings to residences from expected lower piping repair and service needs is about $7/year less than the present $35/year estimate.

In association with this process, city policy changes have been recommended. These include encouraging the use of less corrodible pipes, such as cement lined steel and ductile iron, for distribution systems. The use of asbestos cement and galvanized pipes is discouraged for municipal, industrial, or commercial use. The use of copper or plastic pipe for residential piping is encouraged, as is the use of low-lead solder and glass lined water heaters.

Factors other than cost that influenced the decision to use this process included the potential impact on industrial water use. Area firms are adjusted to the relatively mineral free water presently supplied. Use of the low carbonate process should only slightly affect ion-exchange units or carbon adsorption beds, and few industries are expected to need extensive adjustments. The waste water discharged into Puget Sound should have lower metals concentrations, as will the waste water sludge. The corrosion abatement process is presently being further tested and fine tuned, and a 21 month plan, design, permit acquisition, and construction time period is anticipated.

Carroll County, Maryland

Carroll County, Maryland is a formerly rural area located about 30 miles northwest of Baltimore that has experienced a large population increase in the last two decades. The county currently has about 13,000 residences that rely on individual wells for domestic water, and being built since the early 70's, many of these houses contain copper piping joined with 50% lead solder. The major geologic formations supplying the well water include the Triassic Sandstone, the Wakefield Marble, and the Pretty Boy Schist. The sandstone waters are of variable pH, the marble waters are neutral or higher, but the bedrock acidity of the schist formation produces low pH waters.

In November, 1975, a 45 unit apartment complex served by two wells was found to have a 0.34 ppm lead concentration in a daytime water sample. At the same time, several children living in the complex were found to have moderately elevated blood lead levels. The complex consisted of relatively new buildings (two to 14 years old), but the water system neutralzer was poorly maintained and consequently ineffective. The neutralzer problem was corrected, lead concentrations dropped to below the federal standard of 0.05 ppm, and the children's blood levels returned to normal over a period of a few months.

A year later, in another part of the county, the physician of a family experiencing a gastro-intestinal illness thought their drinking water might be contaminated. A bacteriological analysis was negative, but the water's pH of 5.5 coupled with an inspection of the type of plumbing used in the house, suggested heavy metal contamination. Sampling indicated lead levels of 1.8 ppm and copper levels of 7.9 ppm in the tap water. Subsequent sampling of 14 new houses in this subdivision showed that 12 houses had lead concentrations greater than 0.05 ppm and 10 houses had copper concentrations in excess of 1.0 ppm in early morning samples. A second sampling, after water had run for five minutes, showed six houses with lead levels in excess of the federal standard. Water sampled directly from the well showed no lead or copper, and homes with a neutralizer that adjusted the water to pH 7.2-7.5 also showed no lead or copper. It was concluded that poor workmanship during the copper piping installation and the use of lead solder had precipitated the problem.

This subdivision incident prompted a random sampling of the tap water in homes in new subdivisions, and when 11 of 35 samples were found to contain lead levels above 0.05 ppm in samples where the water had run for five minutes, The Carroll County Health Department requested investigative assistance from the Center for Disease Control. A subsequent random sampling analyzed 350 homes in the county, determining pH, alkalinity, early morning lead and copper levels, and lead and copper levels after running the water for five minutes. Test results showed that low pH and low alkalinity were associated with excessive lead and copper levels in the tap waters.

Consequences of this testing included the immediate recommendation that the water, after standing overnight or for long periods, be allowed to run for two minutes prior to use. The plumbing code in the county was revised to permit the use of NSF-approved (grade 14) plastic tubing in new construction and repair work, and a neutralizer to raise water pH above 7.0 is presently recommended in existing homes with copper piping. The calcite filter type of neutralizer is suggested as best for this problem. (31)

Orange County, California

Between July, 1961 and March 1963, 206 houses were built by a land development firm in an area of southern Orange County, California. All plumbing was copper and water was supplied from wells by a local water utility district. A typical water analysis showed calcium, 225 ppm; magnesium, 40 ppm; sodium, 160 ppm; sulfate, 525 ppm; chloride, 170 ppm; bicarbonate, 360 ppm; TDS, 1500 ppm; hardness, 735 ppm; pH 7.1; and free carbon dioxide, 36 ppm.

In January, 1963, a one million gallon reservoir and hydropneumatic tank system began operation to provide better water service to the development's growing population. Some houses had been occupied since the spring of 1962 and had used water pumped directly from the wells. However the problem of perforation leaks in copper tubing throughout the development did not occur until three months after the additional system began operation. In April, 15 leaks were reported, and the rate of about 15 leaks reported per month continued through October.

By May 1963, the builder had decided that the leaks were not the result of faulty workmanship and sought the assistance of consultants, including two corrosion experts, a testing laboratory, and a civil engineering firm. The subsequent investigation determined that the corrosion was a form of severe occasional pitting occurring on the inside surface of the copper tubes. The pipe surface was covered with a thin green layer, assumed to be copper carbonates, and the pits formed conical penetrations into the tube material and were covered by nodules up to 1/8 inch in height. The pitting occurred in a random pattern and was not necessarily found near joints. The copper that had been used was both "Type K" and "Type L", had been supplied by three different manufacturers, and was found to conform to ASTM Specification B88-62 for that material. Copper staining of plumbing fixtures, that may result from copper solubilization in soft, acidic waters, was not found. Leaks appeared in occupied and unoccupied houses, and although electrical services were grounded to the water systems, the unoccupied houses did not have their power turned on. It was also noted that water from the same wells was used in other parts of the utility's service area with few reports of errosion failures.

The consultants decided that the probable cause of corrosion was the combined presence of free carbon dioxide and dissolved oxygen, possibly enhanced by the high TDS concentration. Although the well water had minimal dissolved oxygen, field measurements indicated that a dissolved oxygen concentration of about 3 ppm existed after the water passed through the reservoir and hydropneumatic system. The consequent remedial action taken by the water purveyor was to begin using water from two other wells. Because one of the additional wells had high iron and manganese levels, a package treatment unit consisting of potassium permanganate, caustic soda, and chlorine addition with pressure-type sand filtration was installed. Delivery of the treated water began in September, and the rate of pipe failures dropped to nearly zero in November.

In early 1964, copper tubing failures began to recur. The consultants found that while the well providing water with high iron and manganese concentrations had initially shown low levels of free carbon dioxide, the level had risen to about 25 ppm. Also, the addition of caustic soda that had neutralized the free carbon dioxide, had been discontinued after less than two months of operation. In April, the wells were taken out of service and the delivery of imported water to the affected area began. After about a month, the rate of tube failure again dropped to almost zero.

Damage resulting from the corrosion cost the builder substantial financial losses, bad publicity, inability to sell houses, and the loss of FHA financing commitments. He consequently sued the purveyor for negligence in not reducing the carbon dioxide content of the water and for breach of warranty that essentially says that in the absence of an explicit warranty, a seller warrants his goods to be suitable for the purpose for which they are sold.

The court found that the water only was responsible for the corrosion and that the addition of caustic soda was a simple and inexpensive remedy. However, the water supplier was not found negligent for his failure to reduce the free carbon dioxide concentration in the water. He was found guilty of breach of warranty and the judgment was for the builder's claimed loss. The court ruled that the water was defective in that the purveyor warranted that the water would be reasonably fit for transmission through copper pipes and would not damage or corrode the tubing during its normal life expectancy.

Additional Corrosion Control Practices

The Catskill-Delaware water system supplying New York City is treated with fluosilic acid for fluoridation that lowers the pH of this soft water from 6.9 to 6.3. Caustic soda is then added to raise the pH to the 6.9-7.2 range. The effectiveness of this system has been judged on the basis of consumer complaints, with an increase in the number of complaints of green (copper) staining occurring when insufficient caustic soda was added. Samples of water at consumer taps by the New York City Health Department indicated that of 500 samples analyzed for lead, copper, and iron, only a few cases of lead in excess of 0.05 ppm were found, contrary to the health department's expectations (40).

In New London, Connecticut, severe corrosion problems experienced prior to 1969 have been controlled by pH adjustment and corrosion inhibitor addition. The raw water pH of 6.8 is adjusted to 7.2-7.5 and zinc orthophosphate is added to produce a 0.5 mg/l zinc concentration in the water. Tap water sampling has shown this treatment to effectively control lead and copper concentrations.

Other large metropolitan areas with corrosion control methods are Salem-Beverly, Massachusetts (lime and zinc metaphosphate); Long Beach, California (see October, 1970 issue of JAWWA); Middlesex, New Jersey (see August, 1974 issue of JAWWA); Waterbury, Connecticut; and Philadelphia's Schuylkill River Plant.

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SECTION 7

CONSIDERATIONS FOR CORROSION CONTROL REGULATIONS

Detailed information is presented in this study which presents the nature and magnitude of corrosion and corrosion control in the water works industry. From the results of previous studies as presented in the literature, it is obvious that corrosion control is quite complex and development of a responsible corrosion control strategy for the water works industry requires a comprehensive approach. The objective of this Section is to summarize the information presented in the preceeding Sections through the use of charts and tables to provide the necessary basis for this comprehensive approach. Information presented in these tables is developed directly from data provided and discussed in this study. In as much as results of studies presented in the literature are often in conflict and disagreement and the fact that factors affecting corrosion and corrosion rates are most commonly synergistic, the information and comments provided in these tables should be considered as guidelines only. Additionally, in the interest of brevity to present a comprehensive and readily usable overview, comments and statements have been taken out of context and could be misleading to users lacking sufficient technical understanding of the nature of corrosion in the water works industry. Therefore, it is suggested that references be made to the respective sections of this study, as needed, for effective use of the tables.

The tables and information presented in this Section were selected and organized to follow a logical order for considering and developing a corrosion control strategy for the water works industry. The various materials and their specific use within the water works industry are first presented. Second, the general extent of each material's use as well as the respective associated potential contaminants are presented. This information is presented to help assess the significance of corrosion or deterioration of the various materials and can be used to assign priority for corrosion control strategies if desired. Once materials and their specific potential contaminants have been identified, applicable corrosion monitoring and detection techniques can be selected to determine the extent, if any, of corrosion. The third table is perhaps the most comprehensive and provides a brief summary of the various water quality and conditions of service parameters' effects on corrosion of each of the materials. This table can be used most effectively to assess the potential for controlling all corrosion in a system by comparing the preferred water quality and conditions of service to minimize the corrosion of each material. Finally, a table is presented which identifies and summarizes the applicability of corrosion prevention technologies for each material. The following is a brief description of each of the tables included.

Table 45, Materials and Their Application in the Water Works Industry, identifies specific uses of materials and attempts to provide a relative quantification of occurrance. Specific uses include in-plant systems (piping and appurtenances), transmission lines, storage, distribution mains, service lines, and household plumbing. Information in this table can be used to assist in identifying the types of materials currently in place as well as their relative quantity. This table does not, however, identify current use patterns.

Table 46, Significance of Corrosion or Deterioration of Various Materials Used in the Water Works Industry, presents a brief discussion of the known extent of use of each material as well as the contaminants that have been found to be associated with the use of each material. Concentrations of contaminants released are provided where values are reported in the literature. The importance of this table is its use for assessing corrosion significance of each material. It should be noted here, that it appears from this table that the use of lead and asbestos-cement should be of paramount concern as these two materials occur extensively within the industry and have been associated with releasing significant quantities or concentration of contaminants, lead being potentially toxic and the effects of asbestos fibers in drinking water yet to be determined. Additionally, it should be noted that it is estimated that one-third of all water distribution pipe currently being sold in the U.S. is manufactured of asbestos-cement pipe. Alternatively, lead pipe is currently being used less extensively but, owing to its relatively long life, many of the lead lines installed remain in service. Lead based solders continue to be used extensively.

Table 47, Preferred Water Quality and Conditions of Service to Minimize Corrosion of Materials Used in the Water Works Industry, is the most comprehensive table and provides a brief overview of the factors influencing or affecting corrosion of each material. Water quality parameters included are pH, hardness, alkalinity, dissolved oxygen, carbon dioxide, total dissolved solids, metal ions, and organic acids. Conditions of service included are velocity and temperature. This table can be used to assess the potential of controlling various parameters to control the corrosion within a water system which contains a variety of materials. It should be noted that pH, hardness, and alkalinity are the most controllable water quality parameters using conventional water treatment practices. The other water quality parameters are more difficult to control and/or maintain throughout a distribution system but are included herein to emphasize their synergistic affects on corrosion of materials. The effects of water velocity can only be controlled through design, and possibly, operation practices.

In general, water pH should be maintained near neutral or in the slightly alkaline range. However, it is noted that localized corrosion has been observed to peak in plain iron in the pH range of 6-9.

For most materials, the effect of hardness concentration is synergistic with other parameters. In general, hard waters are considered less aggressive then soft water to materials with the exception of aluminum in which the reverse is true. For iron-based materials, the presence of calcium ions has been shown to control corrosion if sufficient alkalinity exists. However, hardness concentrations do not appear to influence corrosion characteristics of stainless steel. In the case of copper, it has been found that soft waters may not be corrosive if the carbon dioxide concentration is low while pitting corrosion has been observed in cold hard water indicating that hardness concentration does not act independently on the corrosion or pitting of copper.

Corrosion and pitting appear to be inhibited in waters containing higher alkalinity concentrations for most materials except copper. In copper pipes, the addition of bicarbonate has been shown to actually enhance corrosion under specific conditions. Desired alkalinity concentration ranges of 20 mg/l or higher for lead pipes (12) and 40 mg/l or higher for concrete pipes (25) have been reported. For asbestos-cement materials, the aggressiveness of water is defined as a function of the combined levels of pH, hardness, and alkalinity concentrations. Although good studies on the pH effect on asbestos-cement independent of the other factors is lacking (12), a less "aggressive" water should be produced by increasing any one of the three factors.

Dissolved oxygen concentrations cannot be controlled or maintained effectively throughout a water system. Nevertheless its presence or absence can significantly affect corrosion or corrosion rates on various materials and is therefore included in Table 47. In all cases with the metals, a low concentration of dissolved oxygen is desirable to minimize corrosion. However, a higher dissolved oxygen concentration is generally desirable for the formation of protective films. For the iron-based materials, corrosion appears to increase linearly with increased dissolved oxygen concentration. For copper, however, the presence of dissolved oxygen is known to enhance corrosion, but corrosion or the corrosion rate is not dependent on the dissolved oxygen concentration. Little information is provided in the literature identifying the effects of dissolved oxygen concentration on nonmetallic materials.

As with dissolved oxygen concentrations, low carbon dioxide concentrations are desirable to minimize corrosion. For lead materials, it has been stated that the presence of excess carbon dioxide concentration will tend to dissolve protective carbonate films and assist corrosion.

Results of studies reported in the literature indicate that the effects of total dissolved solids (TDS) concentrations on corrosion of the metals is complex and no general characterization can be established. For plain iron it has been reported that while the presence of TDS can decrease dissolved oxygen and carbon dioxide concentrations resulting in a reduction in corrosion, the increased conductivity can, in fact, increase the range of galvanic coupling or lead to the formation of less protective films. It is also stated in the literature that the presence of chloride (Cl^-) and sulfate ($SO_4^=$) ions can increase corrosiveness of water while elsewhere (11) it is stated that the presence of these two ions can improve the protectiveness of scale.

For galvanized iron, it is reported that chloride ion concentrations observed in most potable water supplies do not increase corrosion or corrosion rates while higher concentrations will tend to accelerate corrosion. For the case of stainless steel, the literature reports that the presence of sulfate ions will inhibit corrosion while the presence of chloride ions can cause severe corrosion.

The corrosive effects of metal ion concentrations also varies with the specific material as well as with the specific metal ion. The presence of copper ions has been reported to be a major factor affecting and increasing the corrosion of galvanized steels. Additionally, the presence of copper, tin, nickel, and mercury have been shown to be detrimental to the corrosion of aluminum. Conversely, low concentrations of iron (Fe^{++}) have been reported to inhibit corrosion in copper and to precipitate on asbestos-cement to form a protective coating inhibiting calcium leaching (3).

Little information is presented in the literature describing the corrosive effects of the presence of organic acids. For iron-based materials, it is reported that the presence of humic acids can improve protective deposit formation and lead to reducing corrosion or the corrosion rate (30, 40). Alternatively for lead, the literature recommends that the occurrance of organic acids whose lead salts are soluble should be minimized to prevent corrosion (32). It is also reported that the occurrence of an unidentified high molecular organic acid found in surface but not in ground water may inhibit corrosion in copper piping (5).

For most materials used in the water works industry, it is reported that both stagnant waters and waters of high velocity will promote corrosion. Where protective coatings may be formed, some flow is required. However, excessive velocities can cause impingement attack and accelerate corrosion. In general, but not in all cases, water velocities ranging between 2-7 fps are desirable.

Temperature effects on the corrosion of materials are of most concern at elevated temperatures above that observed from operations at a utility. With the exception of aluminum, increased water temperatures will generally increase corrosion of materials used in the water works industry. Water temperatures in excess of 40°C are considered preferable for minimizing corrosion on aluminum. For plain iron, it is reported that the aggressiveness of water increases with temperatures up to approximately 80°C and then decreases at higher temperatures.

Table 48, Application of Corrosion Control Mechanisms, provides a summary of the various corrosion control alternatives and their application to the various materials. Corrosion control alternatives include both coatings and linings and inhibitors. Coatings and linings are coal tar, cement mortar, epoxy, vinyl, and miscellaneous non-coal tar paints. Inhibitors include calcium carbonate, silicates, and phosphates. Cathodic protection is also included as it is applied for protection of the inside of steel tanks.

TABLE 45

MATERIALS AND THEIR APPLICATION IN THE WATER WORKS INDUSTRY

MATERIAL	IN PLANT SYSTEMS: PIPING	IN PLANT SYSTEMS: APPURTENANCES	TRANSMISSION LINES	STORAGE	DISTRIBUTION MAINS	SERVICE LINES	HOUSEHOLD
WROUGHT IRON	✓				✓	✓	✓
CAST/DUCTILE	✓✓	✓✓	✓✓		✓✓✓ (cast iron)	✓	✓
STEEL	✓		✓	✓✓	✓	✓	✓
GALVANIZED IRON	✓				✓	✓	✓
STAINLESS STEEL		✓✓					✓
COPPER	✓	(brass)				✓✓✓	✓✓
LEAD		✓ (gaskets)	✓		✓	✓	✓
ALUMINUM		✓					✓
ASBESTOS-CEMENT	✓		✓✓		✓✓	✓	
CONCRETE	✓	✓	✓✓	✓✓	✓		
PLASTIC	✓			✓	✓	✓✓	✓✓

KEY: ✓✓✓ Used >50% for the particular service.
✓✓ Frequently used for the particular service.
✓ Has been or is used for the particular service.

TABLE 46

SIGNIFICANCE OF CORROSION OR DETERIORATION OF VARIOUS MATERIALS USED IN THE WATER WORKS INDUSTRY

MATERIAL	EXTENT OF USE	ASSOCIATED CONTAMINANTS
IRON-BASED MATERIALS:		
PLAIN IRON	Cast iron is used in 75% of all major U.S. water supply distribution systems (17). Also used in water appurtenances and treatment plants. Over 1/2 million steel water storage tanks exist in the U.S.	Iron concentrations in excess of the 0.3 mg/l approval limit occur, resulting in ferric oxide (red water) complaints.
GALVANIZED IRON	Generally limited to service lines, in plant systems, and households. It requires threaded joints and gooseneck connections and is declining in usage.	Zinc concentrations will increase 5 to 10 mg/l after 8 to 40 hour exposure to new galvanized pipe. Small amounts of iron will enter solution. Cadmium and lead (impurities in galvanizing process) concentrations will rise.
STAINLESS STEEL	Seldom used for piping, but used where low maintenance and reliable, continuous service is desired, such as pumps, valves, meters, venturis, and pressure regulators.	Besides iron, other metals used to manufacture stainless steel that may enter the water through pitting or corrosion are chromium, nickel and molybdenum.
COPPER	Extensively used in household piping and service lines. From World War II to 1972, over 6 million miles of copper tubing was put into service. Bronze may be used for appurtenances.	Copper, as well as iron, zinc, tin, and lead from associated pipes and solder may be oxidized into solution. Cu concentrations do not raise above about 5 mg/l. Impurities in brasses, such as manganese, arsenic, antimony, phosphorus, bismuth, and tin may also leak out.
LEAD	Little documentation available; according to Donaldson in 1924 (9) approximately 50% of water distribution systems in the U.S. had lead lines, used primarily for service lines and solders for copper pipes; ≈60% of residences in Boston are serviced with lead lines.	Lead concentrations ranging up to ≈ 3.0 PPM from both lead lines and lead based solders have been reported.
ALUMINUM	Use of aluminum is relatively limited; currently used for weir gates, storage tands, reservoir roofs and supports, hot water systems, and pipe lines.	No information available which identifies or quantifies potential contaminants; could release traces of copper, magnesium, silicon, iron, manganese, chromium, zinc, or titanium as well as alumina ions.
ASBESTOS-CEMENT	Approximately 1/3 of all water distribution pipe currently being sold in the U.S. is manufactured of asbestos-cement pipe; approximately 200,000 miles has been placed into service.	Asbestos-cement fibers counts in excess of 4.5 million fibers per liter have been observed; tetrachlorethylene concentrations as high as 2500 µg/l (3) have been observed from lined asbestos-cement pipes (22).
CONCRETE PIPE	Extensively used in water distribution (and storage) systems with service life of over 50 years in some locations. About 15% of new water tanks are concrete	Contaminant release is greatest when the pipe is first used and decreases thereafter. Water hardness and pH initially increase. Oxides of silicon, aluminum, iron, magnesium, and sulfur may hydrolyze, releasing these elements.
PLASTIC PIPE	Currently growing in use for service lines and household piping except in hot water systems; 1978 use was about 1/3 of all piping on a footage basis. Recent development has produced larger pipes being used in distribution mains.	Lead stabilizing compounds may be leached from PVC pipes. Other contaminants arise from the solvents used and include 2-butanone (MEK) and tetrahydrofuran (THF).

TABLE 47

PREFERRED WATER QUALITY AND CONDITIONS OF SERVICE TO MINIMIZE CORROSION OF MATERIALS USED IN THE WATER WORKS INDUSTRY

MATERIAL	pH	HARDNESS	ALKALINITY
IRON-BASED MATERIALS: PLAIN IRON	Long term: Little effect for pH 4-10 except localized corrosion may peak at pH 6-9 range (39). Short term: pH effects are a function of flow rate and time (10).	Calcium (Ca^{++}) inhibits corrosion in the presence of sufficient alkalinity.	1. Greater alkalinity produces less aggressive water (34). 2. Anodic dissolution of iron is accelerated by bicarbonate HCO_3^- through the localized formation of $Fe(CO_3)^{=}$ (7).
GALVANIZED IRON	1. Corrosion rate increases inversely with pH. 2. Optimum pH range is 7-12.	Hard waters are less aggressive than soft waters (21, 37).	Greater alkalinity produces less corrosive waters.
STAINLESS STEEL	Little effect within range of water systems	Not necessary for protection.	Increased bicarbonate alkalinity will inhibit pitting.
COPPER	1. A pH >7 will minimize uniform corrosion; also uniform corrosion will decrease with increasing pH (6). 2. Pitting corrosion will proceed at pH levels above 7.	1. Soft waters are not corrosive if CO_2 is low (18). 2. Pitting corrosion can occur in hard waters which are cold (5).	Addition of bicarbonate may increase corrosion (35, 36).
LEAD	1. A pH of 6-9 is preferred to minimize corrosion (13, 20). 2. A pH of 6.5-7.0 is preferred to minimize corrosion (26).	1. A hardness of 10-100 PPM as $CaCO_3$ is preferred (26). 2. A hardness of 125 PPM as $CaCO_3$ is desirable (32).	An alkalinity of 20 PPM is desireable to form a protective film (12).
ALUMINUM	Optimum pH is 7.0-7.5.	1. In general, soft waters are preferred. 2. The preferred concentration is dependent on the period of immersion. 3. $CaCO_3$ concentration should be approximately equal to the chloride concentration (2).	-
ASBESTOS-CEMENT	pH + Log (Hardness x Alkalinity) should be ≥12.0 (3).		
CONCRETE PIPE	pH levels of 7.0 and greater are preferred to inhibit leaching.	Hardness in excess of 16 PPM Ca^{++} is preferred to inhibit leaching.	Alkalinity in excess of 40 PPM a $CaCO_3$ is preferred to inhibit leaching.
PLASTIC PIPE	-	-	-

TABLE 47
PREFERRED WATER QUALITY AND CONDITIONS OF SERVICE TO MINIMIZE CORROSION OF MATERIALS USED IN THE WATER WORKS INDUSTRY (Cont'd)

MATERIAL	DISSOLVE OXYGEN	CO_2	TDS
IRON-BASED MATERIALS:			
PLAIN IRON	Corrosivity increases linearly with dissolved oxygen concentrations, however, better protective films are formed at higher dissolved oxygen concentrations.	Carbonic acid is aggressive to iron (8).	1. Presence of TDS can decrease O_2 and CO_2 content and, therefore, reduce corrosion. 2. An increase in conductivity can increase the range of galvanic coupling or lead to the formation of a less protective $Fe(OH)_2$ film. 3. The presence of Cl^- and $SO_4^=$ can increase corrosiveness (23). 4. The presence of Cl^- and $SO_4^=$ may improve protectiveness of scale (11).
GALVANIZED IRON	Corrosiveness of water increases directly with increased dissolved oxygen concentrations.	Corrosiveness of water increases with CO_2 concentration (38).	1. At levels required for water treatment, Cl^- does not increase corrosion (1). 2. At levels above that required for water treatment, Cl^- will accelerate corrosion. 3. Corrosion is enhanced with higher neutral salt concentrations (39).
STAINLESS STEEL	1. The presence of dissolved oxygen is necessary for the formation of a protective film. 2. The presence of dissolved oxygen is aggressive and encourages corrosion (14, 29, 33).	-	1. The presence of $SO_4^=$ will inhibit corrosion 2. The presence of Cl^- can cause severe corrosion (severity depends on type of stainless steel), (14, 29, 33).
COPPER	1. Corrosion is negligible in the absence of dissolved oxygen (31). 2. The presence of dissolved oxygen will enhance corrosion, but corrosion or the corrosion rate is not dependent on the dissolved oxygen concentration.	Dissolved CO_2 appears to enhance corrosion.	Specific effects are difficult to identify.
LEAD	Lower concentrations favor inhibition of corrosion.	Excess CO_2 may dissolve protective carbonate films and assist corrosion (32).	1. Chlorides should be minimized (31). 2. Ions that form soluble lead salts should be minimized (32).
ALUMINUM	Minimal dissolved oxygen is optimal (28).	-	1. Chloride concentration should approximate the $CaCO_3$ concentration (2). 2. Preferred TDS concentrations are dependent on the period of immersion.
ASBESTOS-CEMENT	-	Low CO_2 concentrations are preferred.	Possible inhibitory effect of dissolved solids.
CONCRETE PIPE	-	Low CO_2 concentrations are preferred.	-
PLASTIC PIPE	-	-	-

TABLE 47.
PREFERRED WATER QUALITY AND CONDITIONS OF SERVICE TO MINIMIZE CORROSION OF MATERIALS USED IN THE WATER WORKS INDUSTRY (Cont'd)

MATERIAL	METAL IONS	ORGANIC ACIDS	VELOCITY
IRON-BASED MATERIALS:			
PLAIN IRON	-	Presence of humic acids will inhibit corrosion (30).	Stagnant waters can cause pitting and localized corrosion; velocities >15 fps accelerates corrosion; optimum velocity occurs between 1 fps and 8-15 fps.
GALVANIZED IRON	Copper even at low concentrations will increase zinc corrosion; the presence of copper is often a main factor in the corrosion of galvanized iron.	Presence of humic acids improves protective deposit formation and reduces corrosion (40).	Velocity differences produce little effect (4).
STAINLESS STEEL	-	-	1. Stagnant waters are corrosive. 2. High velocity can be tolerated.
COPPER	A low concentration of Fe^{++} (0.05-0.5 PPM) may inhibit corrosion.	An unknown organic corrosion inhibitor exists in surface water but not groundwater; this natural inhibitor is probably of high molecular weight and may be an organic acid (5).	1. Some flow is required to form protective Cu_2O film. 2. Velocity in excess of 5 fps can cause impingement attack (19).
LEAD	-	Minimize the occurance of organic acids whose lead salts are soluble(32).	Water should be running, not standing (27).
ALUMINUM	Metal ions, especially copper, tin, nickel, and mercury should be minimized (15,28).	-	Prefer a minimum velocity of 8 fpm (15).
ASBESTOS-CEMENT	Fe^{++} can precipitate to form a protective coating to inhibit calcium leaching (3).	-	Water should be running, not standing (24).
CONCRETE PIPE	Fe^{++} can precipitate to form a protective coating to inhibit calcium leaching (3).	-	Water should be running, not standing (24).
PLASTIC PIPE	-	-	-

TABLE 47.
PREFERRED WATER QUALITY AND CONDITIONS OF SERVICE TO MINIMIZE CORROSION OF MATERIALS USED IN THE WATER WORKS INDUSTRY (Cont'd)

MATERIAL	TEMPERATURE	COMMENTS	
IRON-BASED MATERIALS:			
PLAIN IRON	Aggressiveness of water increases with temperature up to ≈ 80°C; at higher temperatures the aggressiveness decreases (37).	Effects of any single variable are influenced by other parameters, especially the interrelation between pH, temperature, dissolve oxygen, alkalinity, hardness, TDS, and velocity.	
GALVANIZED IRON	Increasing temperature will increase corrosion (16).	Interrelation exists between pH, hardness, temperature, alkalinity, TDS, plus organic acids or other stabilizing agents like phosphates or silicates.	
STAINLESS STEEL	Increased water temperature above 25°C results in a significant increase in pitting susceptibility.	Different types of Stainless Steel have different corrosive tendencies. Cl^- and Dissolve Oxygen are two most important chemical factors in stainless steel corrosion.	
COPPER	Temperature effects are complex but usually not a major factor.	Copper concentration generally does not exceed 5 PPM--may be limited by solubility of reaction product.	
LEAD	Temperatures 20°C and less are preferred for corrosion control (26).		
ALUMINUM	Prefer higher temperatures of 40°C and up (15).	Aluminum corrosion is highly dependent on the period of immersion.	
ASBESTOS-CEMENT	-	-	
CONCRETE PIPE	-	Corrosion control is practiced by minimizing the dissolution of Ca^{++}, often by regulating $CaCO_3$ stability components.	
PLASTIC PIPE	-	1. Corrosion products that have been found are thought to leach from solvents used for joints. 2. No variable cause-effect testing results are available	

TABLE 48. APPLICATIONS OF CORROSION CONTROL MECHANISMS

	LININGS						INHIBITORS					
Surface Material	Coal Tar	Cement Mortar	Epoxy	Vinyl	Misc. Non-Coal Tar Paints		Cathodic Protection	$CaCO_3$	Silicates	Phosphates		
Tanks:												
Concrete												
Steel	✓	✓	✓	✓	✓		✓					
Pipes:												
Iron		✓						✓	✓	✓		
Steel	✓	✓	✓					✓	✓	✓		
Asbestos-Cement				✓				✓				
Reinforced Concrete								✓				
Lead								✓	✓	✓		
Copper								✓	✓	✓		
Plastic												
Galvanized								✓	✓	✓		
Aluminum										✓		

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SECTION 8.0

RECOMMENDATIONS

The U.S. Environmental Protection Agency was mandated by the Safe Drinking Water Act of 1974 (PL 93-523) to safeguard public drinking water supplies and to protect the public health. Under the act, EPA is required to establish and enforce National Drinking Water Regulations which include corrosion by products in the water that pose a threat to human health. Information to form a basis for developing responsible and implementable corrosion control regulations is partially available from results of historical laboratory and field studies reported in the literature since the 1920's. Many of these investigations were conducted to identify and quantify water quality and conditions of service characteristics which influence corrosion of the various materials used in the water works industry. To supplement this data base, the EPA has initiated additional studies. These studies have focused on more clearly defining and quantifying the various aspects of potential corrosion control strategies which can assist in developing a reasonable corrosion control program. Recent primary emphasis has been to determine the magnitude of the problems and to search for both monitoring and corrective actions which can be enforced. Results of these studies have overwhelmingly concluded that the nature of corrosion and possible corrosion control alternatives are extremely complex. Limiting the corrosiveness of water by the use of a universal corrosion index or parameter is not feasible at this time. Instead it appears that corrosion control can only be accomplished through a comprehensively applied program on a community water system case by case basis.

An example of the complexity and effort involved in administering a responsible corrosion control program is provided by the Seattle Water Department. Their approach includes an extensive monitoring program coupled with an attempt to provide a wide range of treatment techniques including the addition of various corrosion inhibitors. Monitoring is continued simultaneously with the application of treatment alternatives to evaluate performance. In some cases. the results of the monitoring programs are not in agreement with, or at least do not reflect the expectations of the laboratory results. From this experience and from the results presented in the literature it is evident that a complicated and potentially expensive program is necessary to insure the success of corrosion control at each community water system. The following procedures outline a comprehensive program for corrosion control for specific water utilities.

1) Identify and quantify the materials used in the respective water works industry.

2) Characterize the delivered water quality with respect to pH, and concentrations of alkalinity, hardness, carbon dioxide, metal ions, total dissolved solids, organic acids, and temperature as a minimum.

3) Identify potential contaminants which would be indicative of corrosion with respect to materials used and water quality characteristics.

4) Develop and implement corrosion control treatment alternatives which may be feasible for the particular system.

5) Continue monitoring to determine effectiveness of corrosion control strategies.

6) Develop guidelines for future construction practices and local plumbing codes.

With an estimated 60,000 public water suppliers, it is evident that to administer or enforce a program, with these requirements and recommendations, on a nationwide scale would be both technically and economically prohibitive. In many cases the treatment plant operators do not have the technical skills nor do the small municipalities have the financial resources to implement an extensive corrosion control program. Because some potential control methods may enhance corrosion in specific instances, corrective action by unskilled personnel may further aggravate an existing problem. It is also important to note that relatively few water suppliers recognize a corrosion problem or consider corrosion control a high priority.

It is recommended that corrosion control regulations be developed which are both technically and economically reasonable and which can be enforced effectively. This recommendation implies that regulations should be developed which would first screen water suppliers to assess the potential for corrosion in their respective systems. Only those systems suspected of having corrosion problems should be required to initiate further investigations and corrective actions.

Specifically, water suppliers should be required to identify and quantify materials and practices used in their respective water systems. For smaller utilities this inventory can perhaps be easily compiled. For larger utilities, an accurate inventory may be impossible to compile. In these cases, an inventory estimate through use of recent records and historical plumbing codes can be made. This approach implies that developed areas within a large municipality can be sectioned with respect to historical growth, and applicable plumbing codes, which were in affect during that development period, can be superimposed on the respective area to provide some estimate. This procedure will require that large municipalities provide an historical review of respective local and state plumbing codes.

Water suppliers should also be required to conduct water quality investigations throughout their systems to assess corrosivity potential. As addressed in this study, water quality parameters which have historically been investigated to evaluate corrosion characteristics of specific materials used in the water works industry are pH, and concentrations of hardness, alkalinity, dissolved oxygen, carbon dioxide, transition metal ions, total dissolved solids, organic acids, and temperature. It is recommended that these water quality parameters be included as a minimum for a water quality characterization portion of a corrosion control program.

The water quality sampling and analysis program must be designed to effectively characterize the water quality conditions within the system. Samples should be taken from both the water source and at locations following treatment before it enters the distribution system. Samples should also be taken at various representative points along the distribution system as well as at consumer taps. It should be recognized, however, that water quality changes may occur as the water passes through the distribution system and these changes may produce erroneous results. For example, as previously discussed, corrosive water passing through asbestos-cement pipe will tend to leach calcium from the pipe and become less aggressive. Corrosive water samples taken from points long distances downstream of asbestos-cement pipe sections may appear non-corrosive.

The water quality data collected, specifically pH, alkalinity, and hardness can be used to develop corrosion indicators such as the Langelier Index and/or the Aggressive Index. Although limited in use, these two indices are apparently the most widely accepted indicators of corrosiveness of water and should be used as appropriate. However, their limitations should be recognized as previously discussed and corrosivity should not be assessed exclusively by these parameters.

Water suppliers which are identified as having conditions susceptible to corrosion should be encouraged to initiate monitoring programs designed in accordance with the results of the materials and practice inventory and the water quality survey. Those utilities which are found to use lead or materials which are sources of contaminants that adversely affect health extensively should be given priority consideration.

Water systems suspect of having corrosion problems should be encouraged to initiate a monitoring and detection program to determine the nature and extent, if any, of corrosion. The design and extent of this monitoring program is contingent on the potential contaminants which can be expected as dictated by the specific materials used. Potential contaminants which are associated with each material are listed in Table 49. It is suggested that non-subjective (i.e. analytical as opposed to visual) monitoring techniques be used and that samples be taken from consumer's taps and distribution mains. Coupon testing and electrochemical techniques should currently be considered only as indicators of corrosion. It is not necessary to monitor for every associated potential contaminant but rather to monitor for only a few. The potential magnitude of the corrosion problem and the staffing and financial resources of specific water suppliers should dictate the extent of the monitoring programs.

After identification of the specific corrosion related contaminants, an applicable treatment technique relating to the material involved and water quality parameters must be devised. Historically, attempts at corrosion control by $CaCO_3$ deposition have been used most often, but corrosion inhibitors or modifications in calcium carbonate control as noted in chapter 6 should also be considered.

Local jurisdictions should respond to corrosion problems by adjusting the local plumbing code to recommend some pipe materials and not allow others to be used. Lead and unlined asbestos cement piping should be reviewed. Plastic pipe is becoming more accepted and appears to resist corrosion, but the possibility of small amounts of potentially harmful organics entering the water should be further researched. Similarly, pipe coatings should be reviewed in relation to the local waters. The low flow resistance of epoxy coatings may be recommended pursuant to research on trace contaminant release.

TABLE 49. MATERIALS AND THEIR ASSOCIATED CORROSION PRODUCTS

Material	Potential Corrosion Products
Iron-based materials	Fe, Cd, Pb, Zn
Copper	Cu, Fe, Zn, Sn, Pb, Mn, As, Sb, P, Bi
Lead	Pb
Aluminum	Cu, Mg, Si, Fe, Mn, Cr,
Asbestos-Cement	Asbestos fibers, and tetrachlorethylene
Concrete	Si, Al, Fe, Mg, S
Plastic	Pb, components of various solvents including 2-butanone (MEK) and tetrahydrofuran

If several pipe materials are corroding, and the products are identified, it may not be possible to engineer a single program to alleviate all of the contaminants. In this case, where it is possible that the solution to one facet of the problem may aggravate another, the primary concerns should be control of those products deemed most detrimental in terms of health effects. Specifically, this would include lead and asbestos fibers. These may not be the easiest contaminants to justify in terms of economics or aesthetics, but their control should be paramount.

Irrespective of corrosion control regulations, the EPA should review local, state, and national plumbing codes and begin assessing the potential for discouraging the use of potentially dangerous materials and practices. Lead and lead-based solders should be seriously considered for discontinuing their extensive use. Although a large quantity of lead pipe is currently in service, its extensive use has begun to decline, but lead-based solders are currently the most widely used solders for joining copper pipers.